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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

Andriessen et al.

Application No. 10/657,894

Filed: September 9, 2003

Art Unit: Unassigned

Examiner: Unassigned

For: PHOTOVOLTAIC DEVICE COMPRISING A 1,3,5-TRIS-AMINOPHENYL-BENZENE COMPOUND

CLAIM OF PRIORITY

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

In accordance with the provisions of 35 USC 119, Applicants claim the priority of the following application:

Application No. PCT/EP02/10120, filed in the European Patent
Office on September 10, 2002.

A certified copy of the above-listed priority document is enclosed.

Respectfully submitted,

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Date: November 6, 2003

CERTIFICATE OF MAILING

I hereby certify that this CLAIM OF PRIORITY (along with any documents referred to as being attached or enclosed) is being deposited with the United States Postal Service on the date shown below with sufficient postage as first class mail in an envelope addressed to: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

Date: _____

11/6/03



Bescheinigung

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten internationalen Patentanmeldung überein.

Certificate

The attached documents are exact copies of the international patent application described on the following page, as originally filed.

Attestation

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet international spécifiée à la page suivante.

Den Haag, den
The Hague,
La Haye, le

17. 10. 2003

Der Präsident des Europäischen Patentamts
Im Auftrag
For the President of the European Patent Office
Le Président de l'Office européen des brevets
p.o.

M. Perrin

Patentanmeldung Nr.
Patent application n.
Demande de brevet n°

PCT/EP 02/10120



Anmeldung Nr.:
Application no.: PCT/EP 02/10120
Demande n°:

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Bezeichnung der Erfindung:
Title of the invention:
Titre de l'invention: PHOTOVOLTAIC DEVICE COMPRISING A 1, 3, 5-TRIS-AMINOPHENYL-
BENZENE COMPOUND

Anmeldetag:
Date of filing:
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Bemerkungen:
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Remarques: Further applicants:

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5. KROON, Jan - Petten, The Netherlands (US only)

PCT REQUEST

GN02097

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V	Designation of States	
V-1	Regional Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	<p>AP: GH GM KE LS MW MZ SD SL SZ TZ UG ZM ZW and any other State which is a Contracting State of the Harare Protocol and of the PCT</p> <p>EA: AM AZ BY KG KZ MD RU TJ TM and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT</p> <p>EP: AT BE BG CH&LI CY CZ DE DK EE ES FI FR GB GR IE IT LU MC NL PT SE SK TR and any other State which is a Contracting State of the European Patent Convention and of the PCT</p> <p>OA: BF BJ CF CG CI CM GA GN GQ GW ML MR NE SN TD TG and any other State which is a member State of OAPI and a Contracting State of the PCT</p>
V-2	National Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	<p>AE AG AL AM AT AU AZ BA BB BG BR BY BZ CA CH&LI CN CO CR CU CZ DE DK DM DZ EC EE ES FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG KP KR KZ LC LK LR LS LT LU LV MA MD MG MK MN MW MX MZ NO NZ OM PH PL PT RO RU SD SE SG SI SK SL TJ TM TN TR TT TZ UA UG US UZ VC VN YU ZA ZM ZW</p>
V-5	<p>Precautionary Designation Statement</p> <p>In addition to the designations made under items V-1, V-2 and V-3, the applicant also makes under Rule 4.9(b) all designations which would be permitted under the PCT except any designation(s) of the State(s) indicated under item V-6 below. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit.</p>	
V-6	Exclusion(s) from precautionary designations	NONE
VI	Priority claim	NONE
VII-1	International Searching Authority Chosen	European Patent Office (EPO) (ISA/EP)

PHOTOVOLTAIC DEVICE COMPRISING A 1,3,5-TRIS-AMINOPHENYL-BENZENE
COMPOUND

Field of the invention

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The present invention relates to a photovoltaic device comprising a 1,3,5-tris-aminophenyl-benzene compound optionally in a cationic form.

10 Background of the invention.

There are two basic types of photoelectrochemical photovoltaic cells. The first type is the regenerative cell which converts light to electrical power leaving no net chemical change behind. 15 Photons of energy exceeding that of the band gap generate electron-hole pairs, which are separated by the electrical field present in the space-charge layer. The negative charge carriers move through the bulk of the semiconductor to the current collector and the external circuit. The positive holes are driven to the surface 20 where they are scavenged by the reduced form of the redox relay molecular (R), oxidizing it: $h^+ + R \rightarrow O$, the oxidized form. O is reduced back to R by the electrons that re-enter the cell from the external circuit. In the second type, photosynthetic cells, operate on a similar principle except that there are two redox 25 systems: one reacting with the holes at the surface of the semiconductor electrode and the second reacting with the electrons entering the counter-electrode. In such cells water is typically oxidized to oxygen at the semiconductor photoanode and reduced to hydrogen at the cathode. Titanium dioxide has been the favoured 30 semiconductor for these studies.

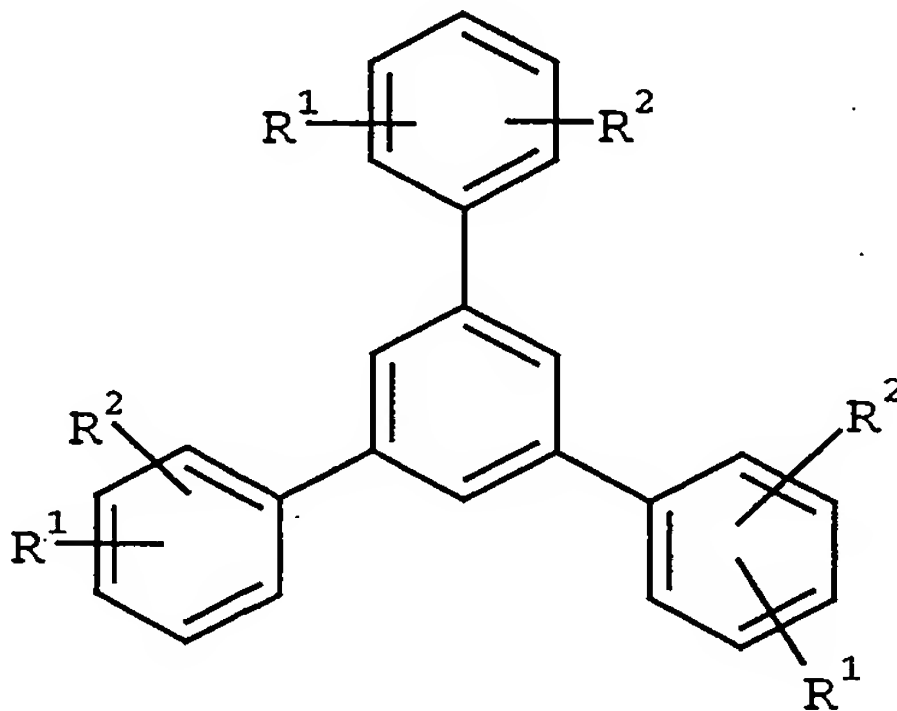
Mesoscopic or nano-porous semiconductor materials, minutely structured materials with an enormous internal surface area, have been developed for the first type of cell to improve the light capturing efficiency by increasing the area upon which the 35 spectrally sensitizing species could adsorb. Arrays of nano-crystals of oxides such as TiO_2 , ZnO , SnO_2 and Nb_2O_5 or chalcogenides such as $CdSe$ are the preferred semiconductor materials and are interconnected to allow electrical conduction to take place. These fundamental techniques were disclosed in 1991 by 40 Graetzel et al. in Nature, volume 353, pages 737-740 and in US 4,927,721, US 5,350,644 and JP-A 05-504023. Graetzel et al.

reported solid-state dye-sensitized mesoporous TiO₂ solar cells with up to 33% photon to electron conversion efficiencies.

EP-A 1 176 646 discloses a solid state p-n heterojunction comprising an electron conductor and a hole conductor,
5 characterized in that it further comprises a sensitizing semiconductor, said sensitizing semiconductor being located at an interface between said electron conductor and said hole conductor; and its application in a solid state sensitized photovoltaic cell.

There is therefore a requirement for thermally stable organic
10 hole-conducting compounds capable of forming stable transparent layers and being compatible with solid state photovoltaic cell configurations.

EP 0 349 034 discloses a chemical compound corresponding to the following general formula:



15 wherein R¹ represents a -NR³R⁴ group, wherein R³ and R⁴, same or different, represents a C₂-C₁₀ alkyl group including said alkyl groups in substituted form, a benzyl group, a cycloalkyl group, or an aryl group, and R² represents hydrogen, an alkyl group including
20 a substituted alkyl group or halogen. Such compounds exhibit hole transport properties as described in 1993 by Novo et al. in 1993 in Phys. Stat. Solidi(B), volume 177, page 223, and by Van der Auweraer et al. in Journal of Physical Chemistry, volume 97, page 8808. In addition such compounds form thermally stable amorphous
25 layers with glass transition temperatures greater than 100°C as reported by Inada et al. in 1993 in Journal of Materials Chemistry, volume 3, pages 319-320. This combination of properties render such starburst compounds particularly interesting for use in organic electroluminescent devices as reported in 1996 by Inada et
30 al. in Mol. Cryst. Liq. Cryst., volume 280, pages 331-336, and in 1997 by Shirota et al. in Journal of Luminescence, volumes 72-74, pages 985-991.

Aspects of the invention.

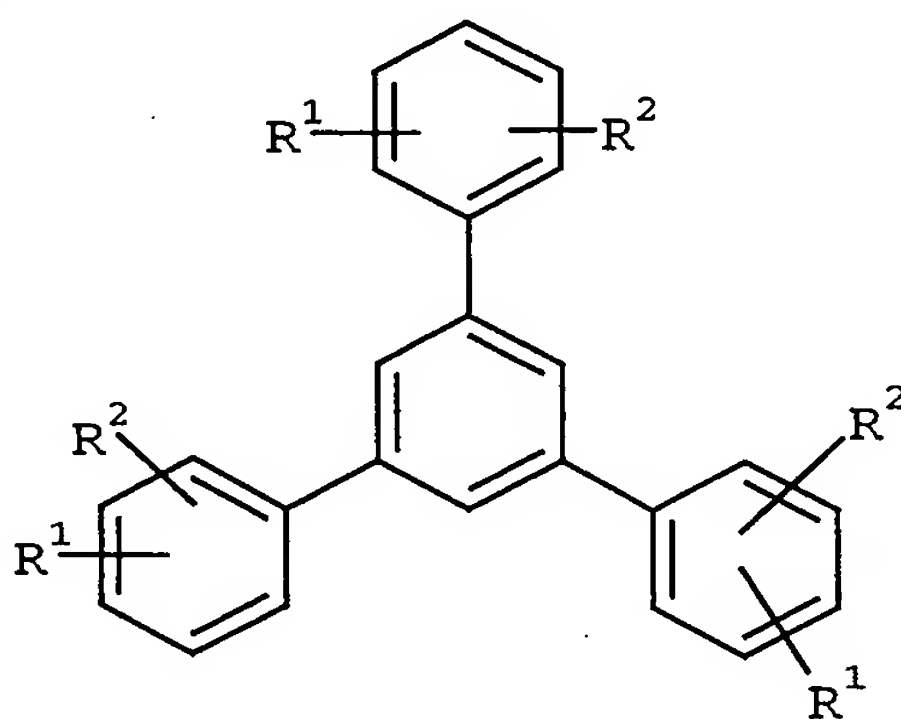
It is therefore an aspect of the present invention to provide a photovoltaic cell with a stable hole-conducting compound.

5 Further aspects and advantages of the invention will become apparent from the description hereinafter.

Summary of the invention.

10 It has been surprisingly found that tris-1,3,5-amino-phenyl-benzene in a cationic form exhibited hole transporting properties which render them compatible with solid state photovoltaic cell configurations.

Aspects of the present invention are realized by a photovoltaic
15 device comprising a n-type semiconductor with a band-gap of greater than 2.9 eV and a 1,3,5-tris-aminophenyl-benzene compound represented by formula (I):



wherein R¹ represents a -NR³R⁴ group, wherein R³ and R⁴, same or
20 different, represents a C₂-C₁₀ alkyl group including the alkyl groups in substituted form, a benzyl group, a cycloalkyl group, or an aryl group, and R² represents hydrogen, an alkyl group including a substituted alkyl group or halogen; and the 1,3,5-tris-aminophenyl-benzene compound is optionally in a cationic form.

25 Aspects of the present invention are realized by a process for preparing the above-mentioned photovoltaic device with at least one transparent electrode comprising the steps of: providing a support with a conductive layer as one electrode; coating the conductive layer on the support with a layer comprising the n-type
30 semiconductor with a bandgap of greater than 2.9 eV; coating the n-type semiconductor-containing layer with a solution or dispersion comprising the 1,3,5-tris-aminophenyl-benzene compound, or cation thereof, to provide after drying a layer comprising the 1,3,5-tris-

aminophenyl-benzene compound; and applying a conductive layer to the layer comprising the 1,3,5-tris-aminophenyl-benzene compound thereby providing a second electrode.

Preferred embodiments are disclosed in the dependent claims.

5

Detailed description of the invention.

Definitions

10 The term chalcogenide means a binary compound containing a chalcogen and a more electropositive element or radical. A chalcogen is an element from group IV of the periodic table including oxygen, sulphur, selenium, tellurium and polonium.

The term "support" means a "self-supporting material" so as to
15 distinguish it from a "layer" which may be coated on a support, but which is itself not self-supporting. It also includes any treatment necessary for, or layer applied to aid, adhesion to the support.

The term continuous layer refers to a layer in a single plane covering the whole area of the support and not necessarily in
20 direct contact with the support.

The term non-continuous layer refers to a layer in a single plane not covering the whole area of the support and not necessarily in direct contact with the support.

The term coating is used as a generic term including all means
25 of applying a layer including all techniques for producing continuous layers, such as curtain coating and doctor-blade coating, and all techniques for producing non-continuous layers such as screen printing, ink jet printing, flexographic printing.

The abbreviation PEDOT represents poly(3,4-ethylenedioxy-
30 thiophene).

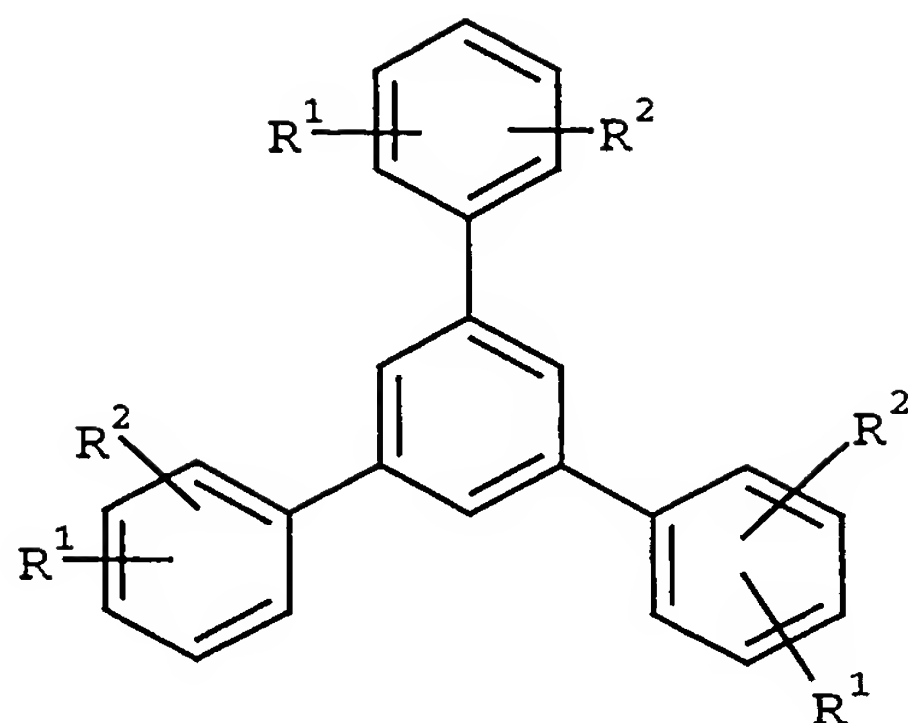
The abbreviation PSS represents poly(styrenesulphonic acid) or poly(styrenesulphonate).

Photovoltaic devices

35

Aspects of the present invention are realized by a photovoltaic device comprising a n-type semiconductor with a band-gap of greater than 2.9 eV and a 1,3,5-tris-aminophenyl-benzene compound represented by formula (I):

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wherein R^1 represents a $-NR^3R^4$ group, wherein R^3 and R^4 , same or different, represents a C_2-C_{10} alkyl group including the alkyl groups in substituted form, a benzyl group, a cycloalkyl group, or an aryl group, and R^2 represents hydrogen, an alkyl group including a substituted alkyl group or halogen; and the 1,3,5-tris-aminophenyl-benzene compound is optionally in a cationic form.

Photovoltaic devices, according to the present invention, can be of two types: the regenerative type which converts light into electrical power leaving no net chemical change behind in which current-carrying electrons are transported to the anode and the external circuit and the holes are transported to the cathode where they are oxidized by the electrons from the external circuit and the photosynthetic type in which there are two redox systems one reacting with the holes at the surface of the semiconductor electrode and one reacting with the electrons entering the counter-electrode, for example, water is oxidized to oxygen at the semiconductor photoanode and reduced to hydrogen at the cathode. In the case of the regenerative type of photovoltaic cell, as exemplified by the solid state Graetzel cell. The charge transporting process can be ionic or electronic.

Such regenerative photovoltaic devices can have a variety of internal structures in conformity with the end use. Conceivable forms are roughly divided into two types: structures which receive light from both sides and those which receive light from one side. An example of the former is a structure made up of a transparently conductive layer e.g. an ITO-layer or a PEDOT/PSS-containing layer and a transparent counter electrode electrically conductive layer e.g. an ITO-layer or a PEDOT/PSS-containing layer having interposed therebetween a photosensitive layer and a charge transporting layer. Such devices preferably have their sides sealed with a polymer or an adhesive to prevent deterioration or volatilization of the inside substances. The external circuit connected to the

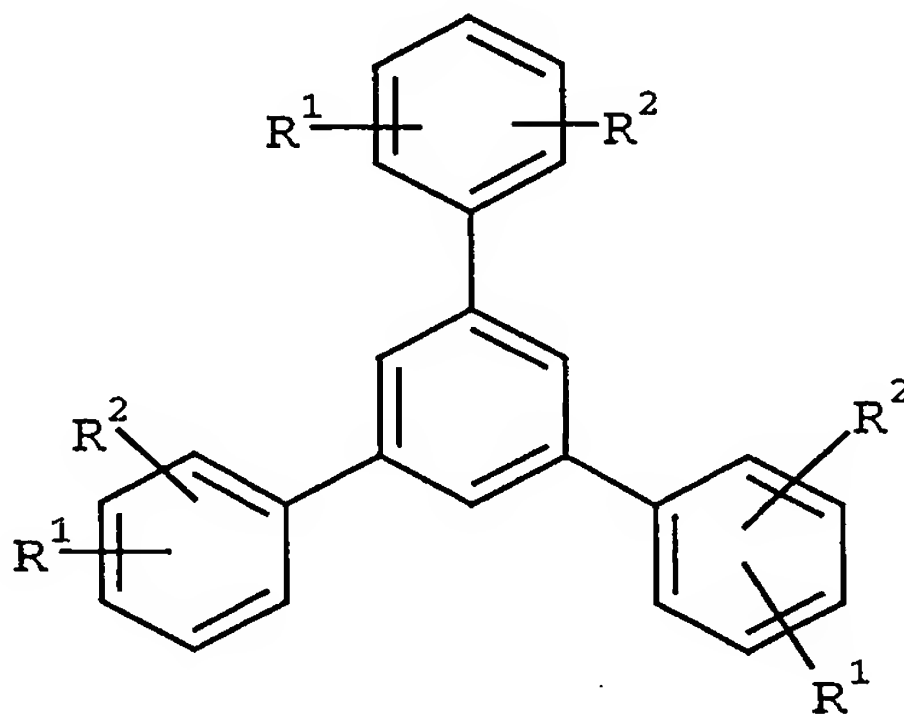
electrically-conductive substrate and the counter electrode via the respective leads is well-known.

According to a first embodiment of the photovoltaic device, according to the present invention, the photovoltaic device
5 comprises a single layer system.

According to a second embodiment of the photovoltaic device, according to the present invention, the photovoltaic device comprises a configuration in which the n-type semiconductor with a band-gap of greater than 2.9 eV is contiguous with the 1,3,5-tris-
10 aminophenyl-benzene compound according to formula (I) or in which a spectral sensitizer is sandwiched between the n-type semiconductor with a band-gap of greater than 2.9 eV and the 1,3,5-tris-aminophenyl-benzene compound according to formula (I).

15 1,3,5-Tris-aminophenyl-benzene compounds

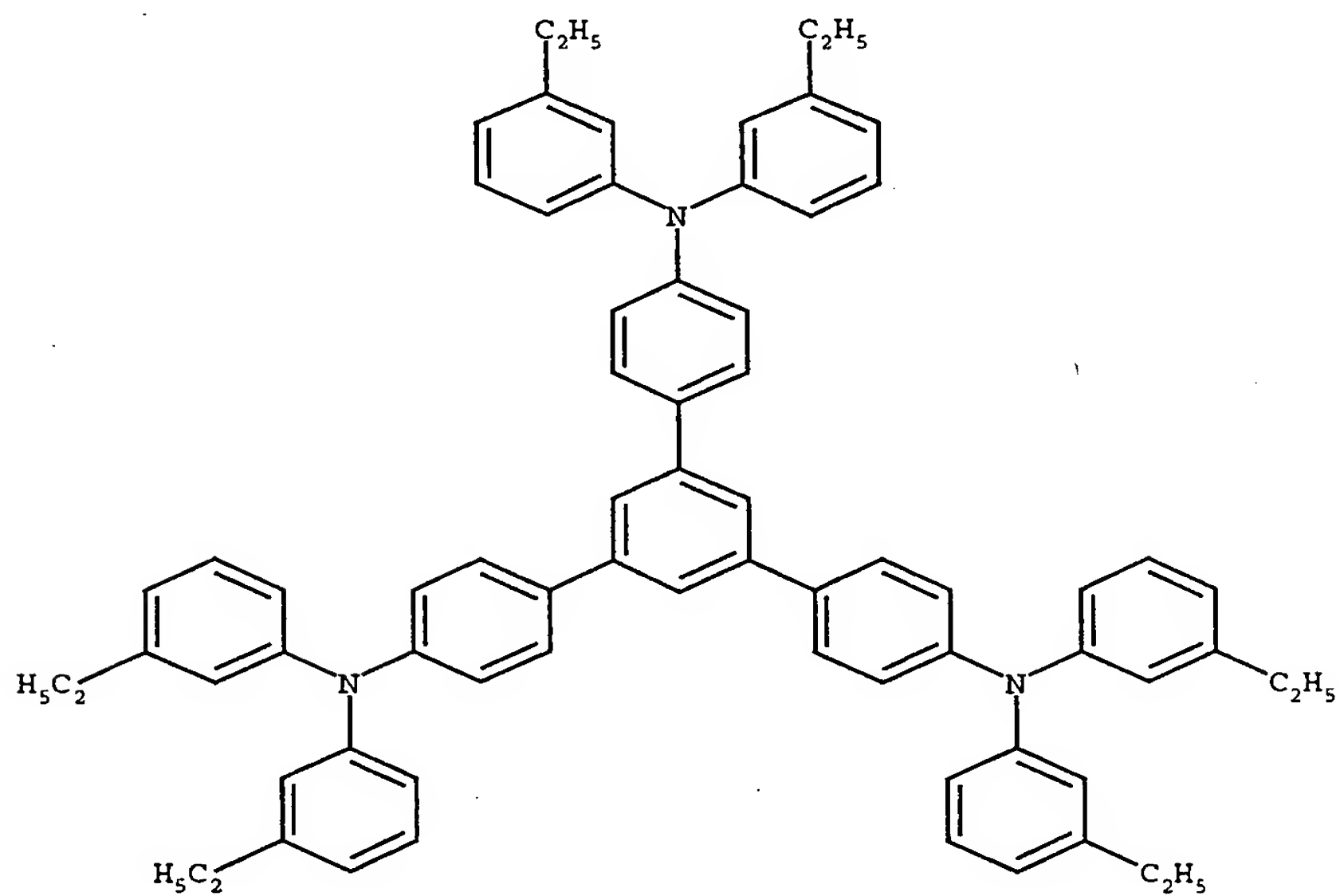
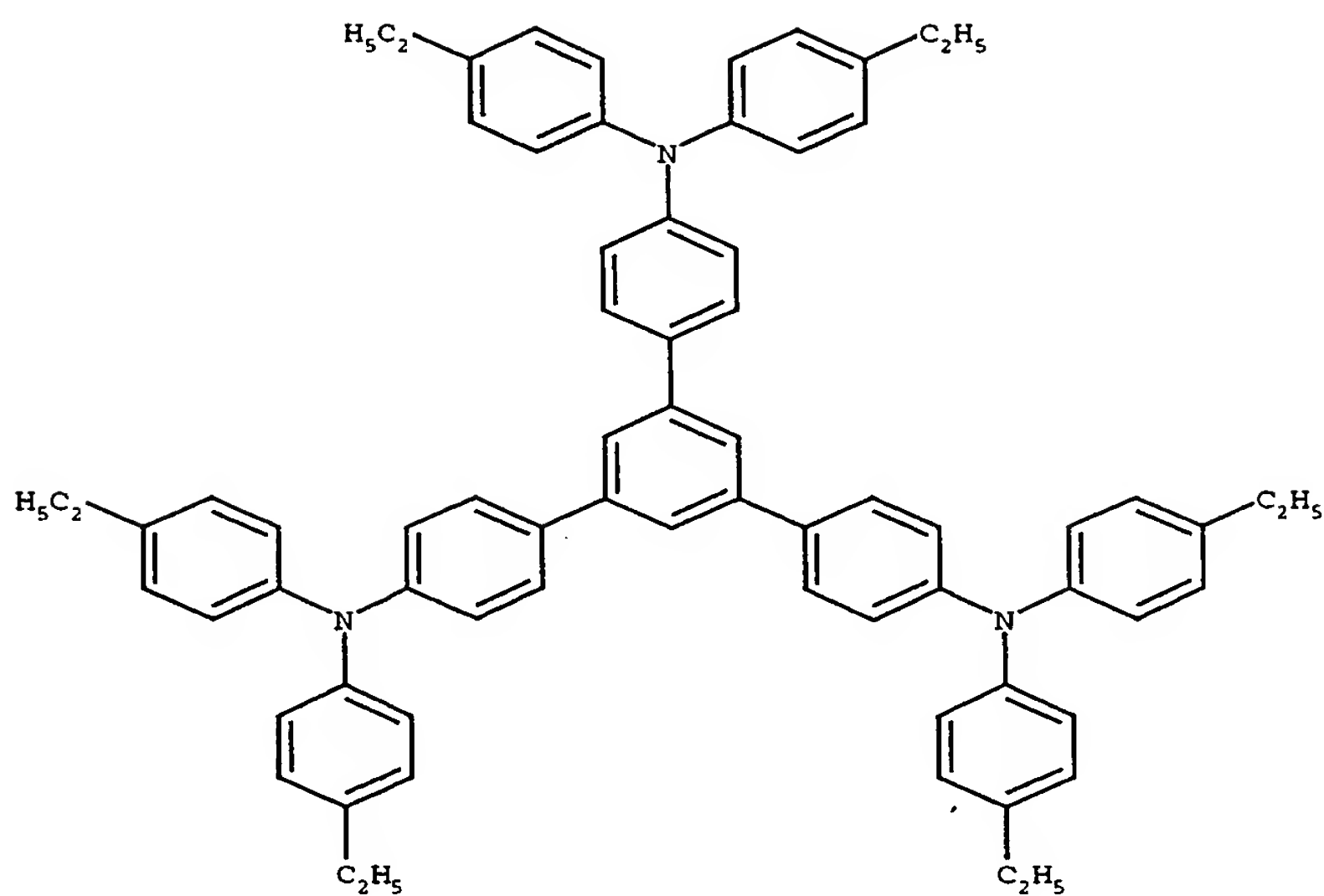
A photovoltaic device comprising a n-type semiconductor with a band-gap of greater than 2.9 eV and a 1,3,5-tris-aminophenyl-benzene compound represented by formula (I):



20 wherein R^1 represents a $-NR^3R^4$ group, wherein R^3 and R^4 , same or different, represents a C_2-C_{10} alkyl group including the alkyl groups in substituted form, a benzyl group, a cycloalkyl group, or an aryl group, and R^2 represents hydrogen, an alkyl group including
25 a substituted alkyl group or halogen; and the 1,3,5-tris-aminophenyl-benzene compound is optionally in a cationic form.

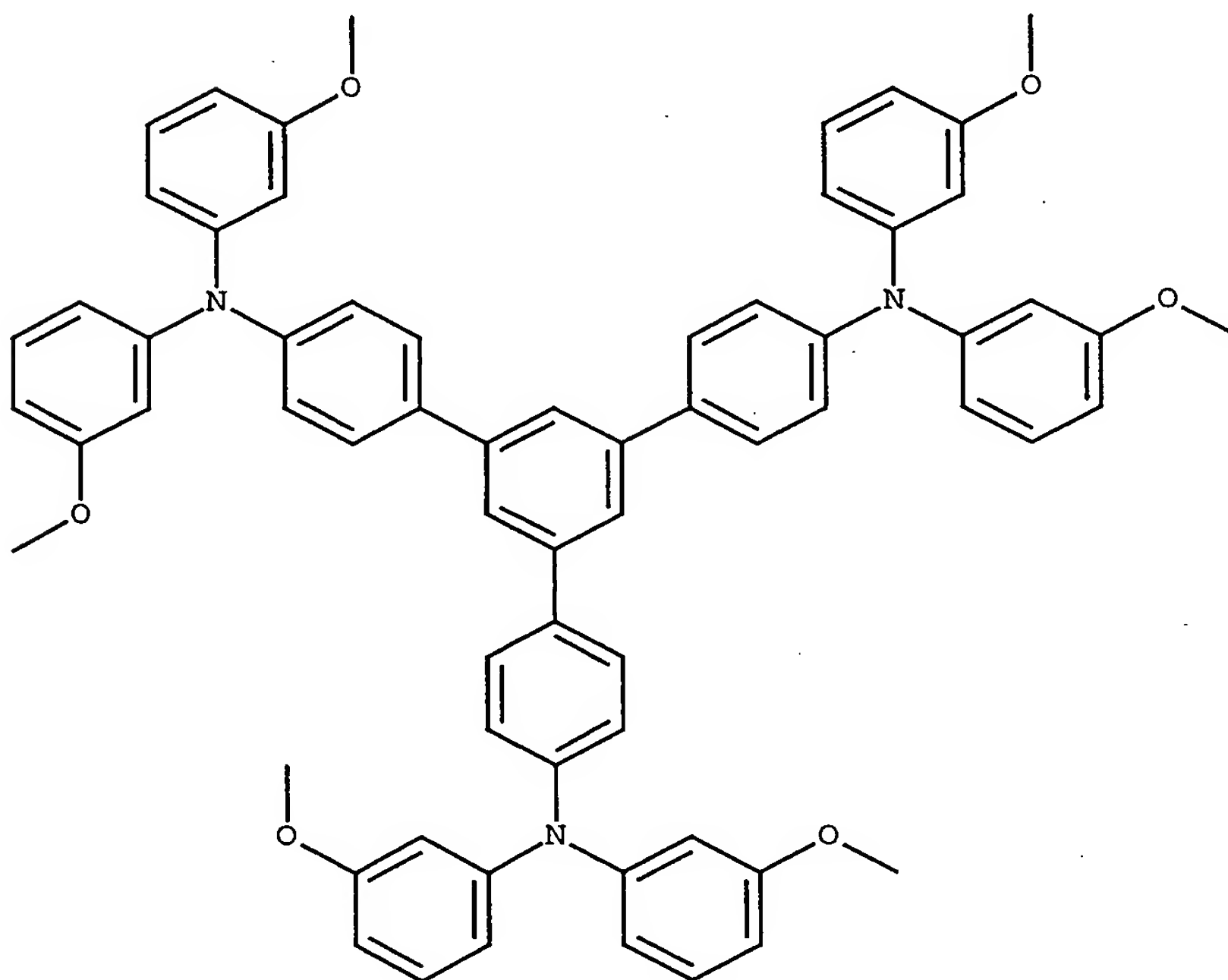
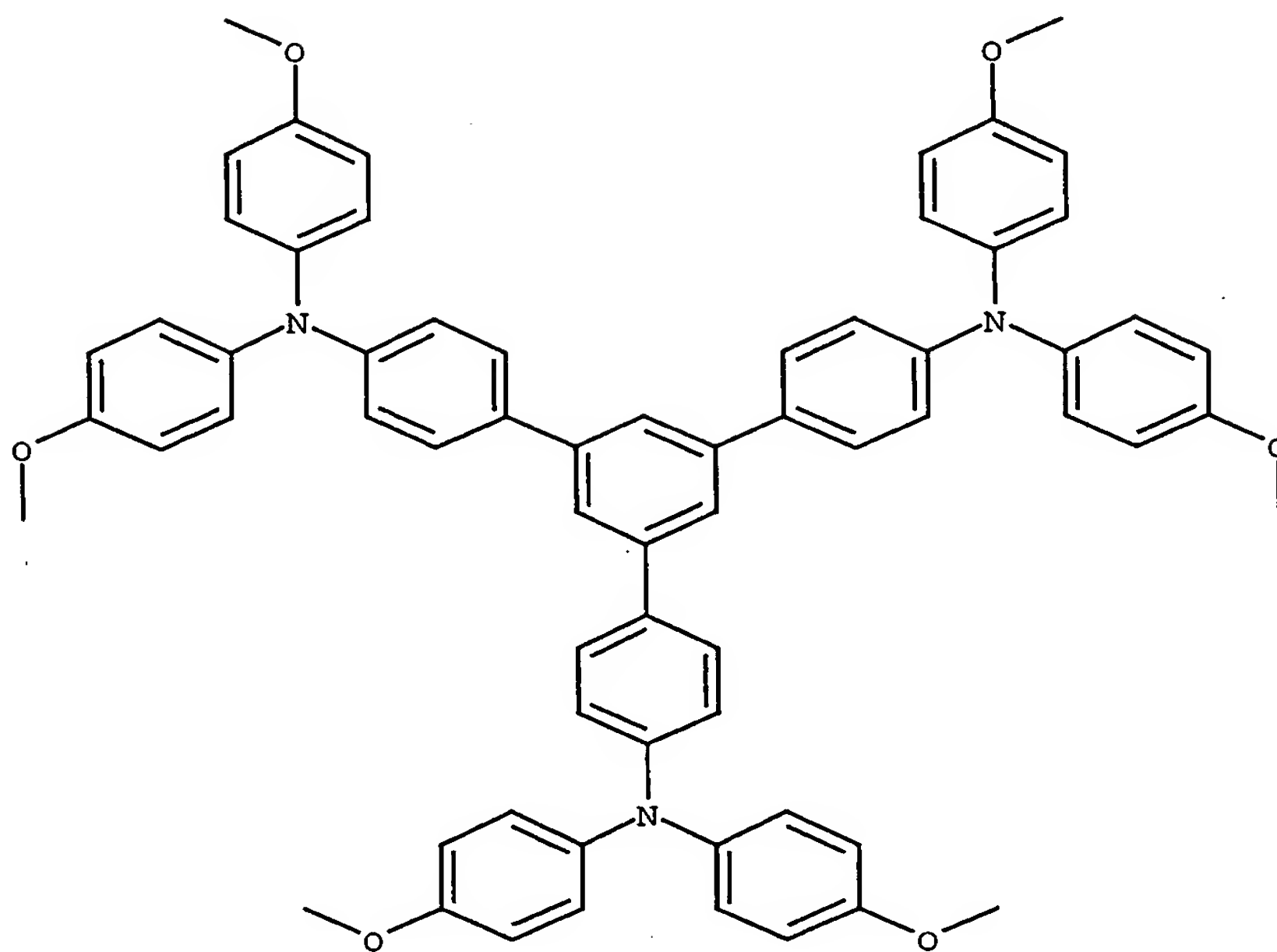
According to a third embodiment of the photovoltaic device, according to the present invention, the 1,3,5-tris-aminophenyl-benzene compound represented by formula (I) is selected from the
30 group consisting of:

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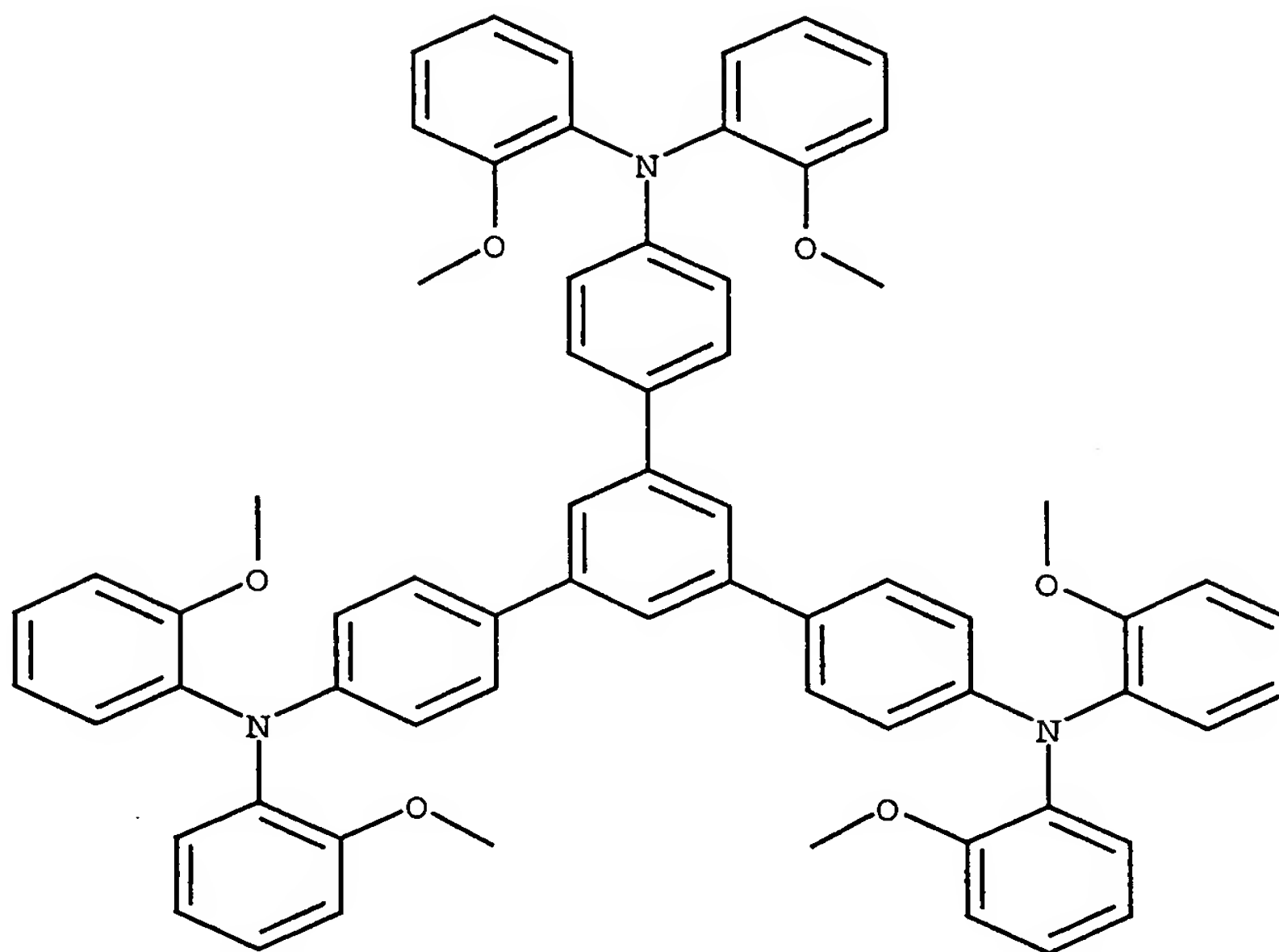
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5

and

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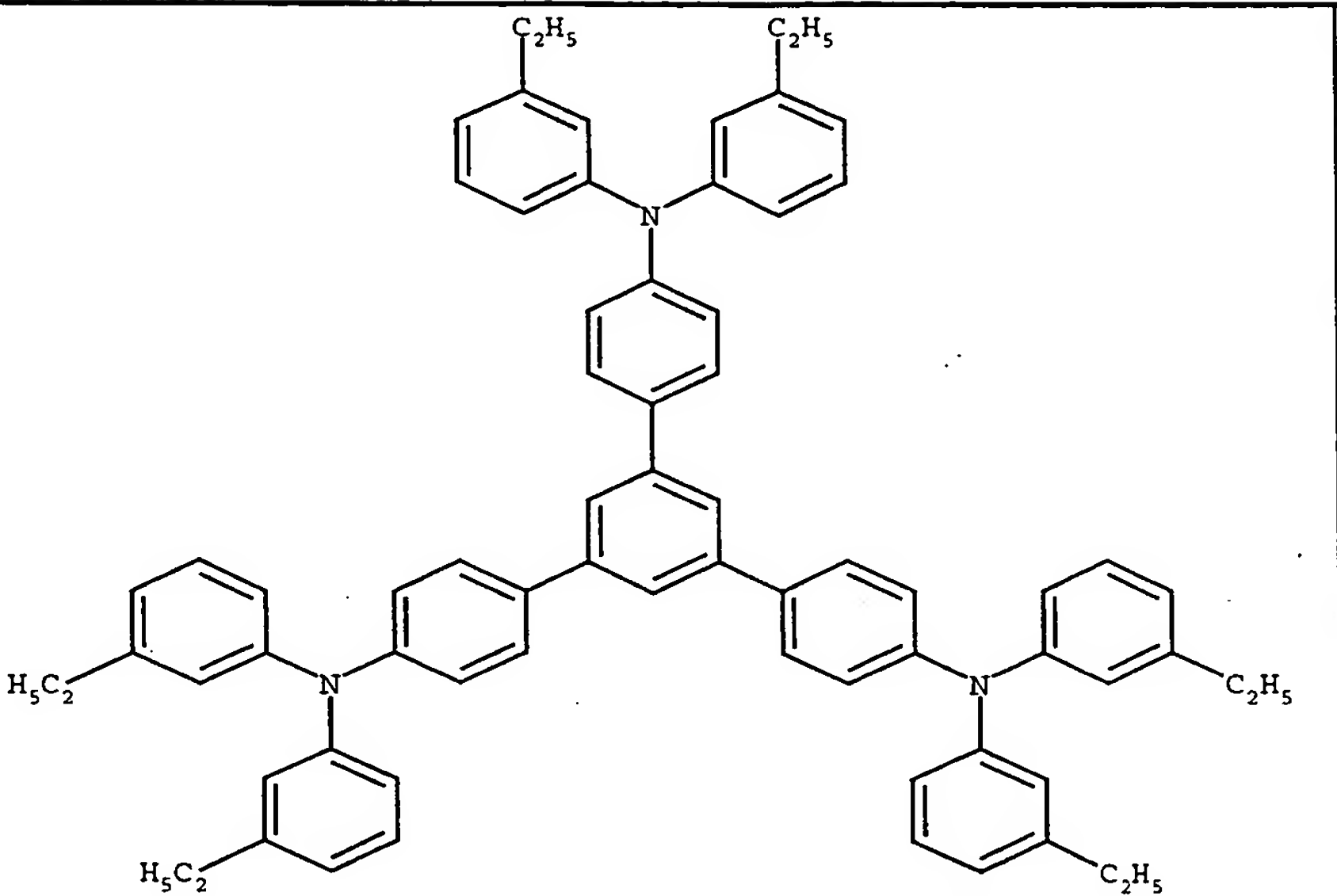
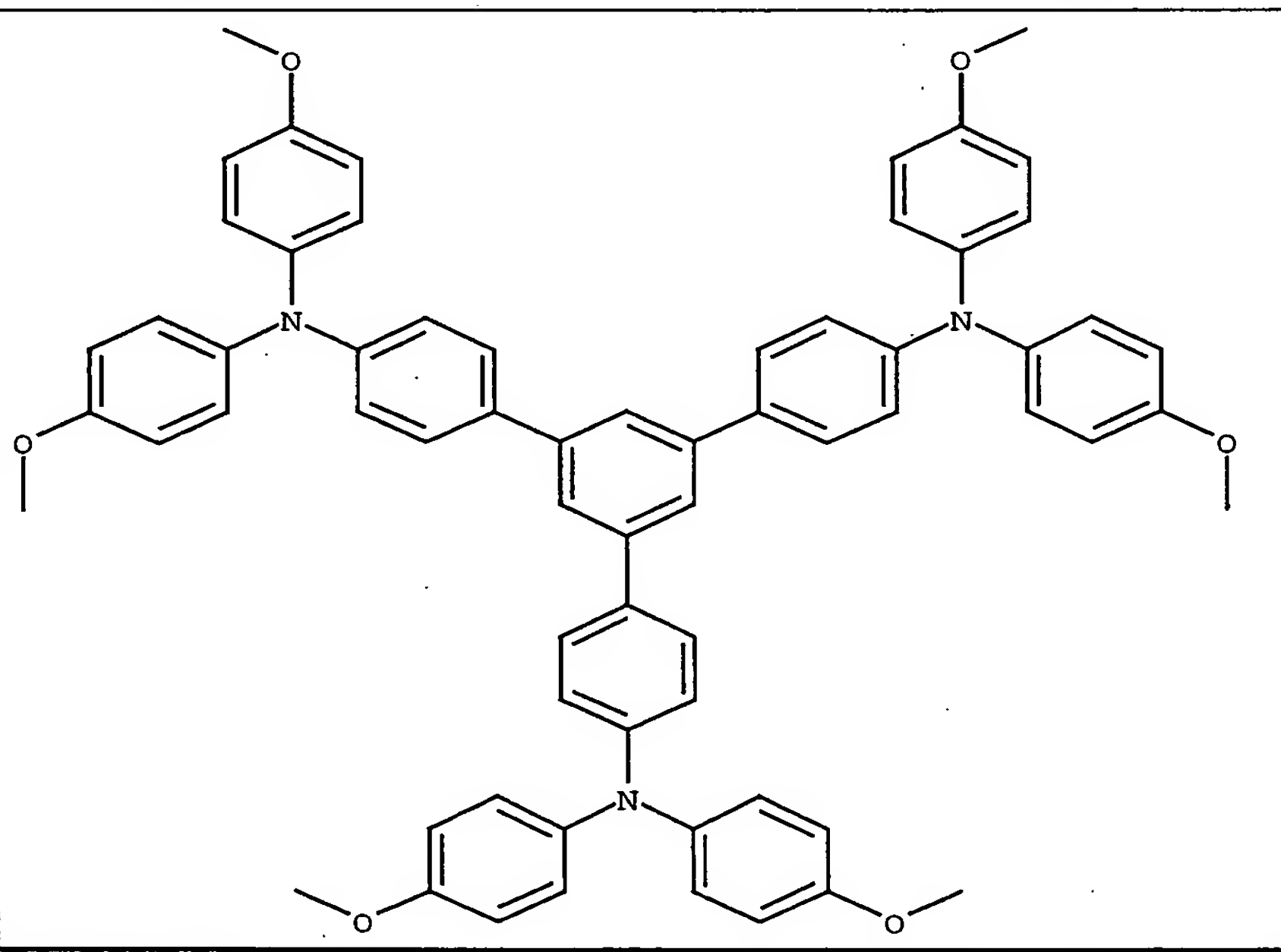


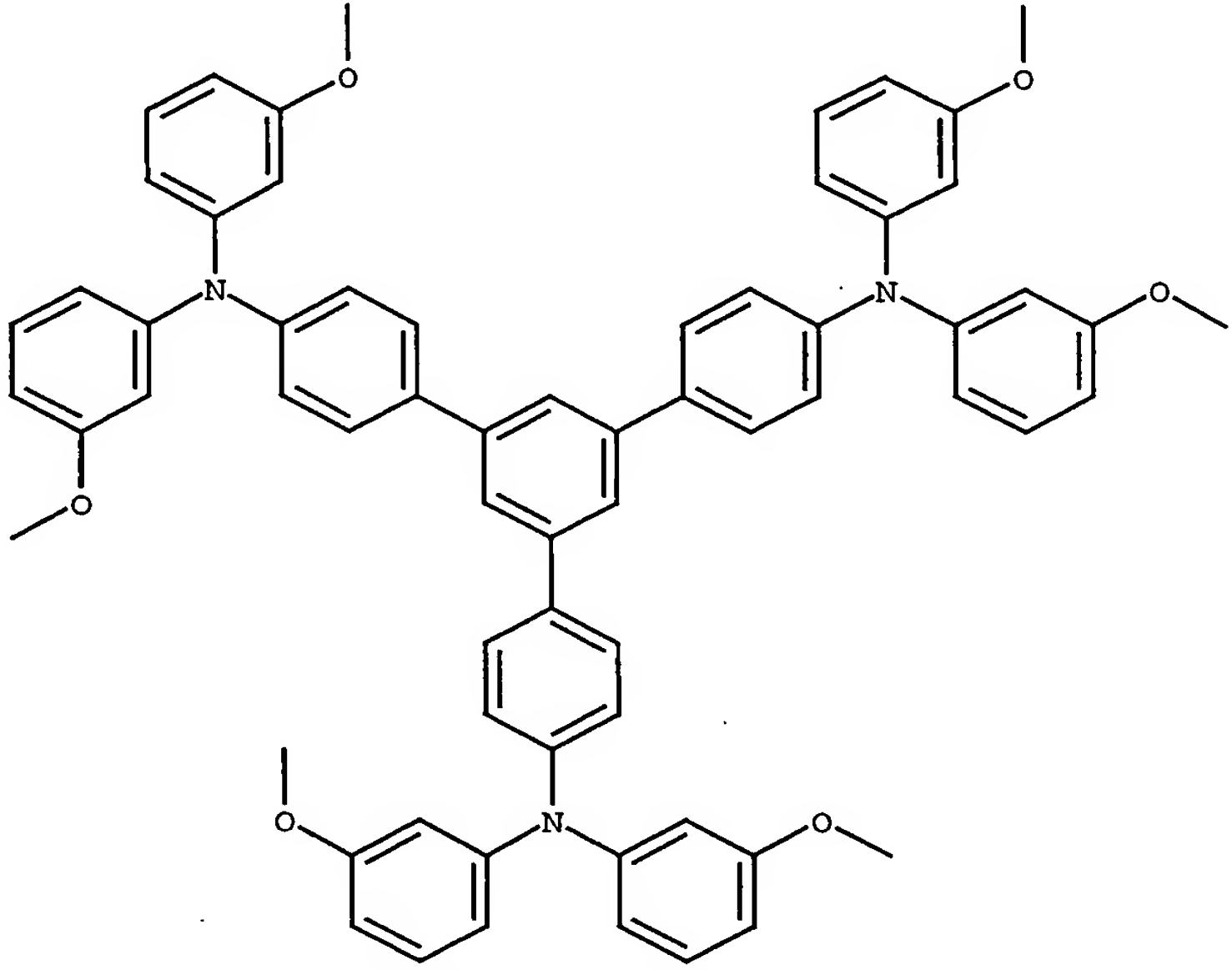
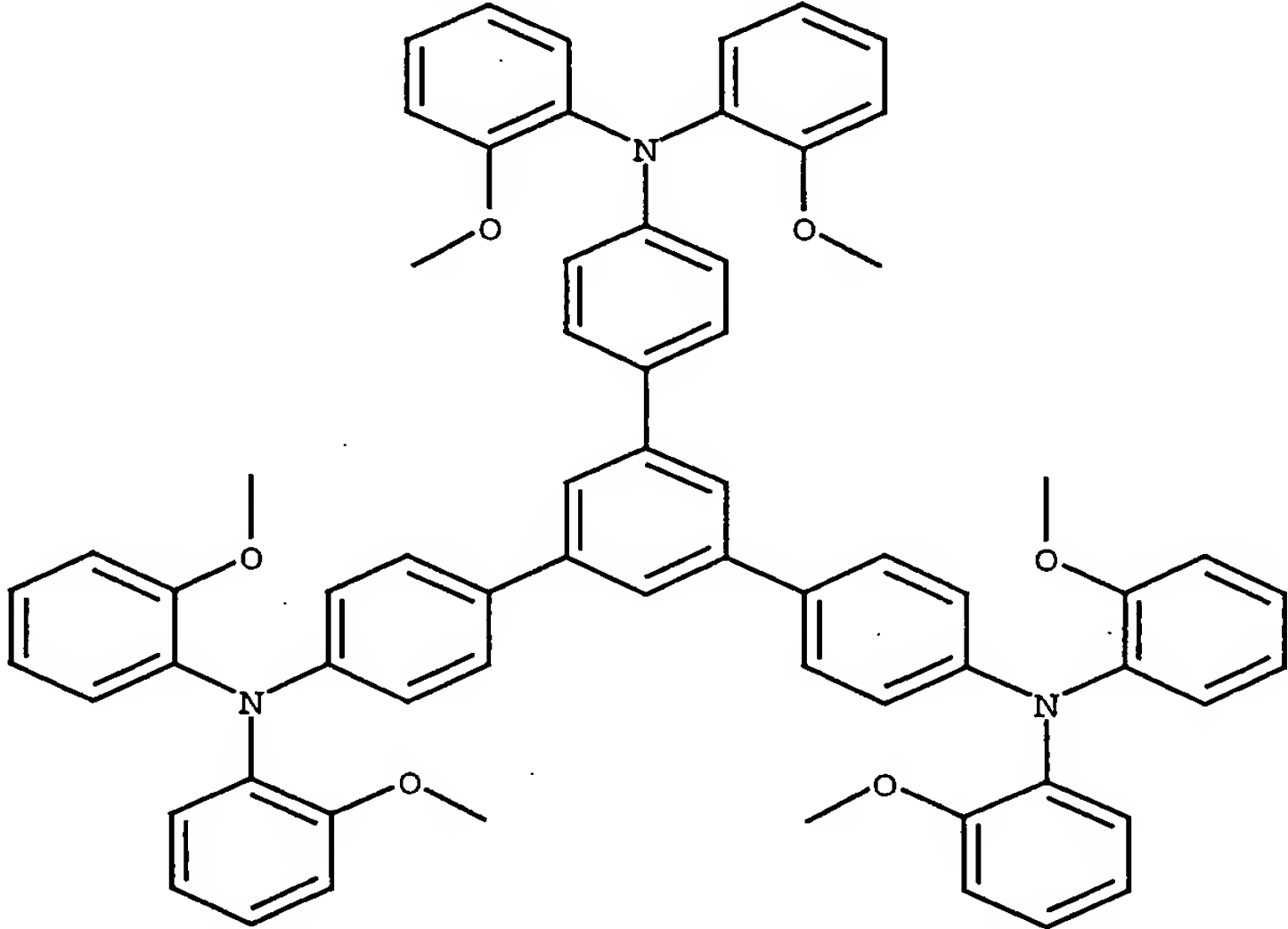
or the cations thereof.

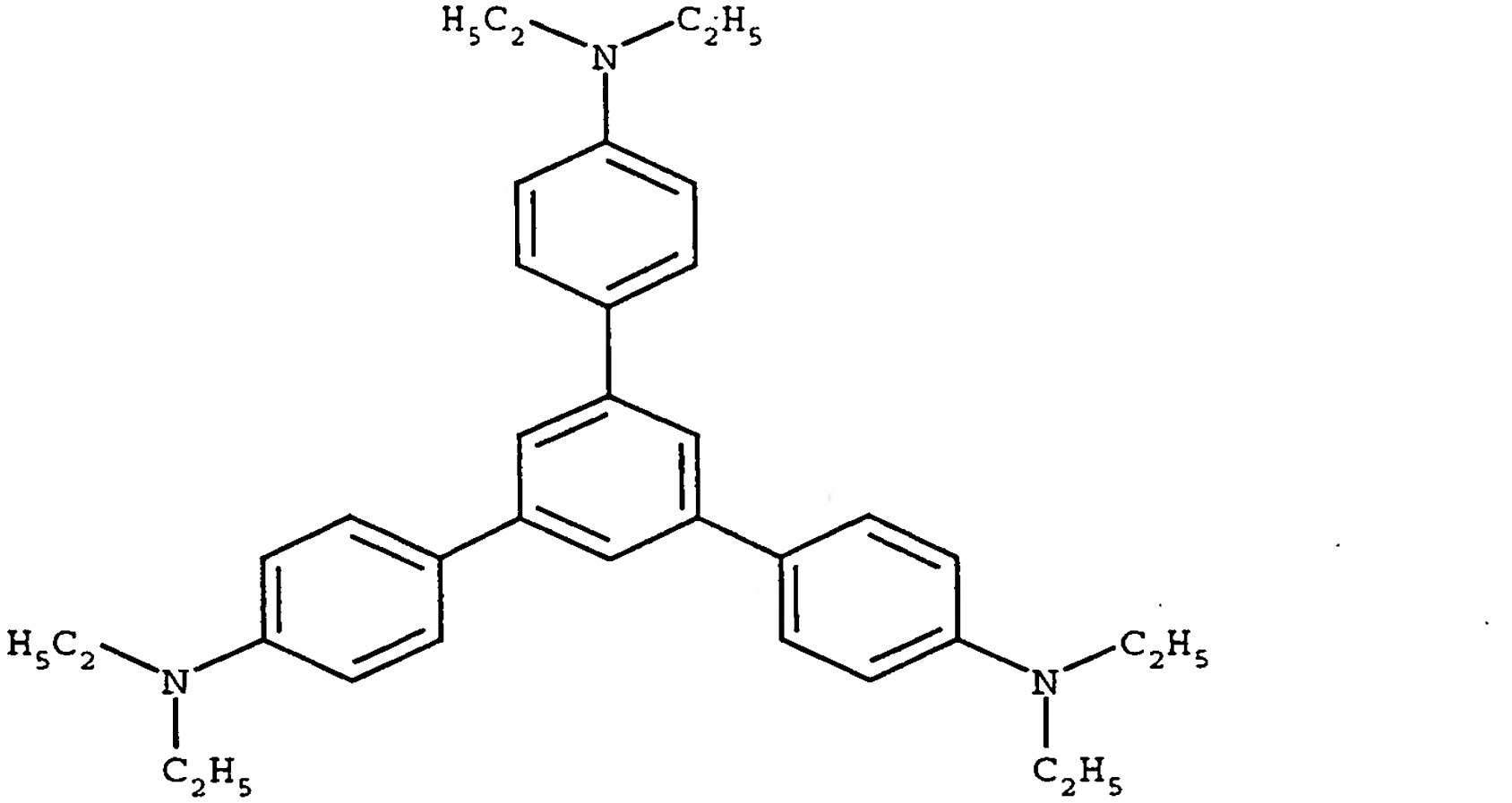
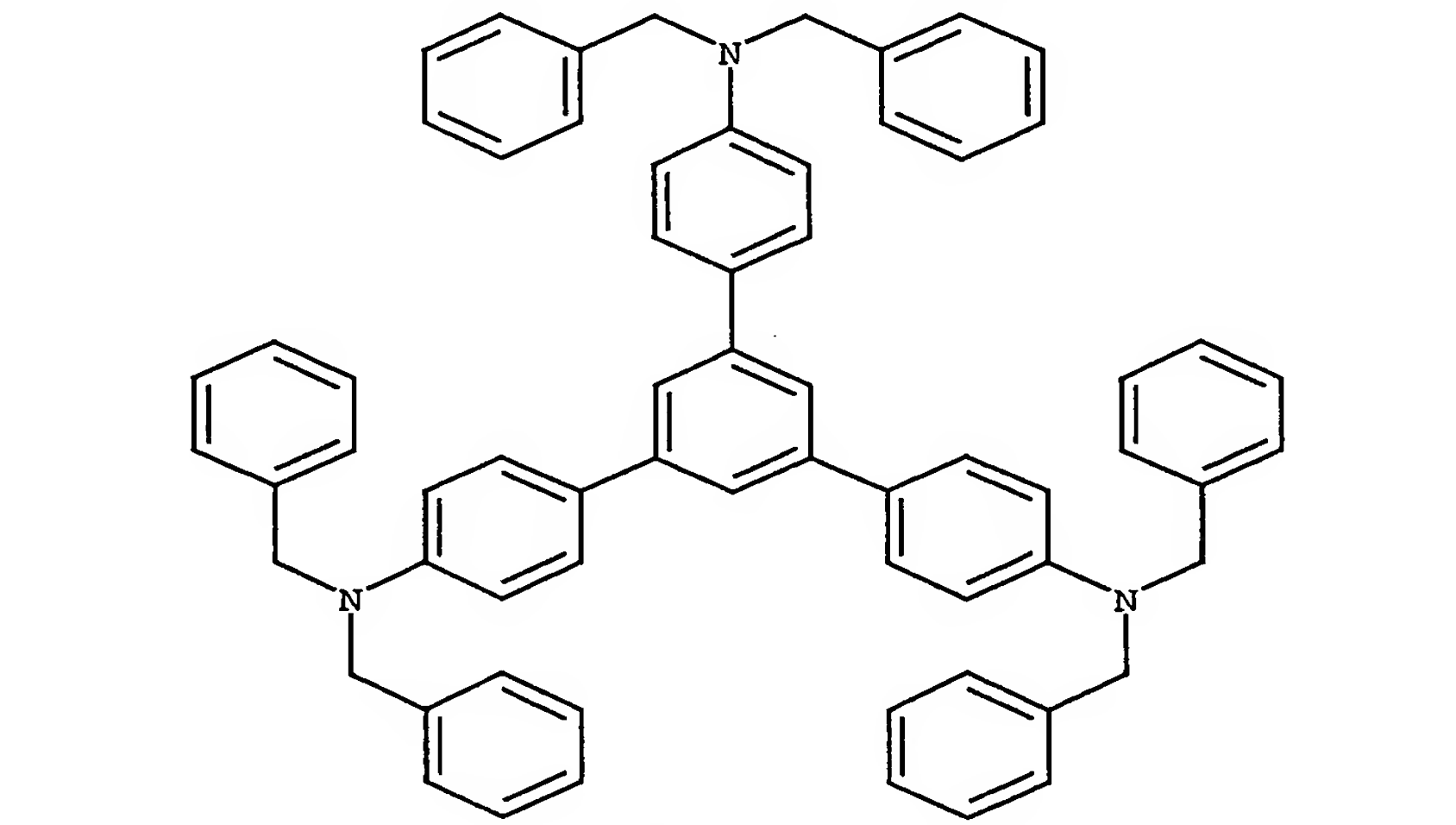
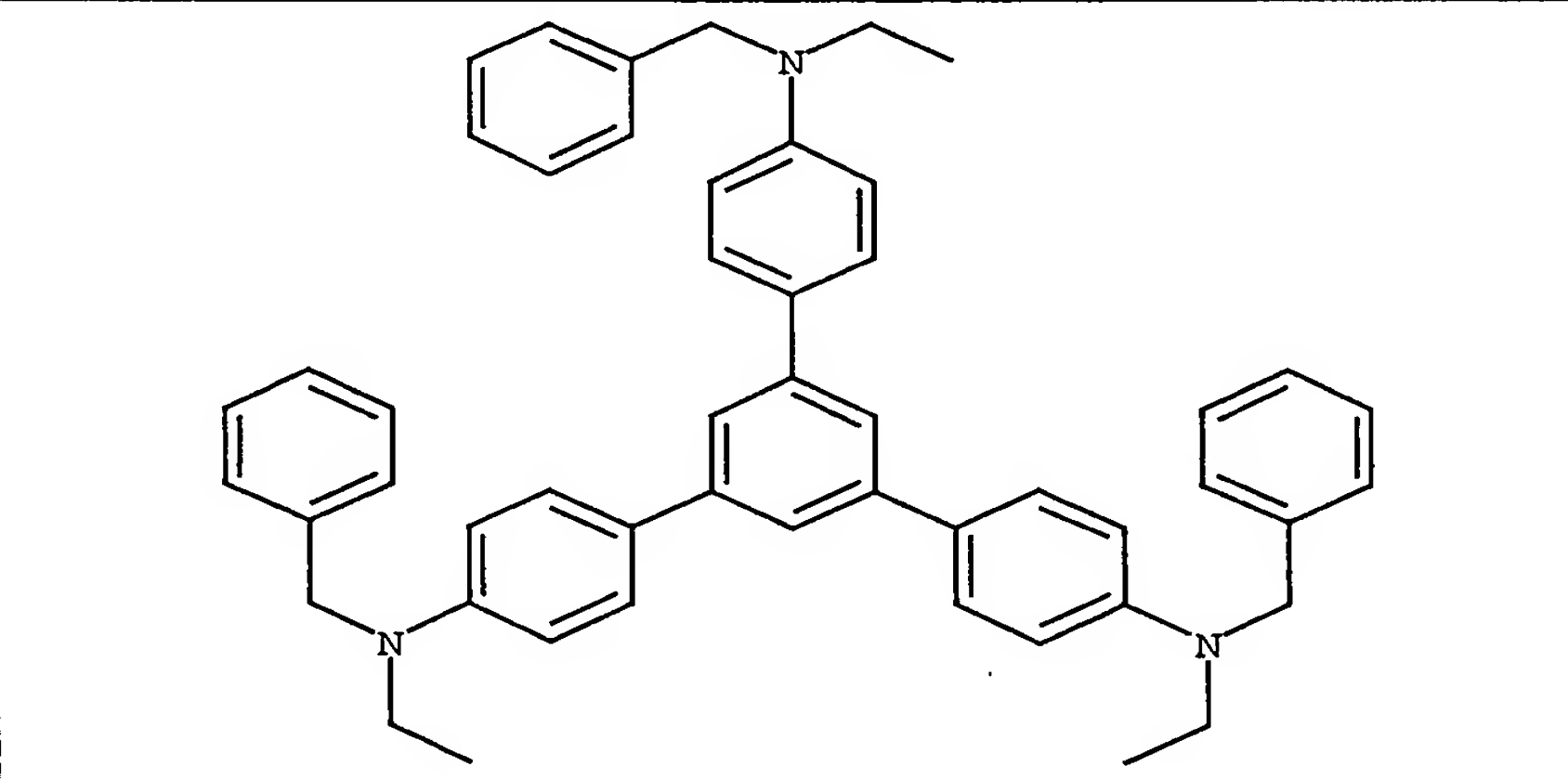
Suitable 1,3,5-Tris-aminophenyl-benzene (TAPB) compounds, according to the present invention, include:

5

TAPB compound		$E^{1/2}_{ox}$ in MeCN vs sce [V] *
TAPB01		0.86

TAPB02	 <chem>CC1=CC=C(C=C1N(C2=CC=CC=C2)C3=CC=CC=C3C4=CC=CC=C4)C5=CC=CC=C5C6=CC=CC=C6N(C7=CC=CC=C7)C8=CC=CC=C8C9=CC=CC=C9C10=CC=CC=C10</chem>	0.90
TAPB03	 <chem>COC1=CC=C(C=C1N(C2=CC=CC=C2)C3=CC=CC=C3C4=CC=CC=C4)C5=CC=CC=C5C6=CC=CC=C6N(C7=CC=CC=C7)C8=CC=CC=C8C9=CC=CC=C9C10=CC=CC=C10</chem>	0.937

TAPB04	 <p>Chemical structure of TAPB04: A central benzene ring is connected at the 1 and 4 positions to two identical side chains. Each side chain consists of a benzene ring connected at its 1 position to a nitrogen atom. This nitrogen atom is also bonded to a 3-methoxyphenyl group and a 4-methoxyphenyl group. The central benzene ring is connected at its 1 position to a benzene ring, which is in turn connected at its 1 position to a nitrogen atom. This nitrogen atom is also bonded to a 3-methoxyphenyl group and a 4-methoxyphenyl group.</p>	0.70
TAPB05	 <p>Chemical structure of TAPB05: A central benzene ring is connected at the 1 and 4 positions to two identical side chains. Each side chain consists of a benzene ring connected at its 1 position to a nitrogen atom. This nitrogen atom is also bonded to a 3-methoxyphenyl group and a 4-methoxyphenyl group. The central benzene ring is connected at its 1 position to a benzene ring, which is in turn connected at its 1 position to a nitrogen atom. This nitrogen atom is also bonded to a 3-methoxyphenyl group and a 4-methoxyphenyl group.</p>	-

TAPB06	 <chem>CCN(CC)c1ccc(cc1)-c2cc(ccc2-c3ccc(N(CC)CC)cc3)-c4ccc(N(CC)CC)cc4</chem>	0.73
TAPB07	 <chem>c1ccc(cc1)CN(Cc2ccccc2)c3cc(ccc3-c4ccc(CN(Cc5ccccc5)Cc6ccccc6)cc4)-c7ccc(CN(Cc8ccccc8)Cc9ccccc9)cc7</chem>	0.855
TAPB08	 <chem>CCN(Cc1ccccc1)c2cc(ccc2-c3ccc(CN(CC)Cc4ccccc4)cc3)-c5ccc(CN(CC)Cc6ccccc6)cc5</chem>	0.810

TAPB09		-
TAPB10		0.805
TAPB11		0.900

TAPB12		0.802
TAPB13		-
TAPB14		-

* reference ferrocene: 0.430 V

TAPB01 has a glass transition temperature of 107°C.

Cations of 1,3,5-tris-aminophenyl-benzene compounds according to formula (I) can be prepared by oxidation of the particular 1,3,5-tris-aminophenyl-benzene compound with an oxidizing agent such as $N(p-C_6H_4Br)_3SbCl_6$.

n-type Semiconductors

According to a fourth embodiment of the photovoltaic device, according to the present invention, the n-type semiconductor has a
5 bandgap of less than 6.0 eV.

According to a fifth embodiment of the photovoltaic device, according to the present invention, the n-type semiconductor is selected from the group consisting of titanium oxides, tin oxides, niobium oxides, tantalum oxides, tungsten oxides and zinc oxides.
10 The n-type semiconductor may be porous or non-porous, although non-porous n-type semiconductors are preferred.

According to a sixth embodiment of the photovoltaic device, according to the present invention, the n-type semiconductor is titanium dioxide.
15

Spectral sensitization of n-type semiconductor layers

According to a seventh embodiment of the photovoltaic device, according to the present invention, the photovoltaic device further
20 contains at least one spectral sensitizer.

According to an eighth embodiment of the photovoltaic device, according to the present invention, the photovoltaic device further contains at least one spectral sensitizer selected from the group consisting of metal chalcogenide nano-particles with a band-gap of
25 less than 2.9 eV and greater than 1.5 eV, organic dyes and metallo-organic dyes.

According to a ninth embodiment of the photovoltaic device, according to the present invention, the photovoltaic device further contains at least one spectral sensitizer selected from the group
30 consisting metal oxides, metal sulphides and metal selenides.

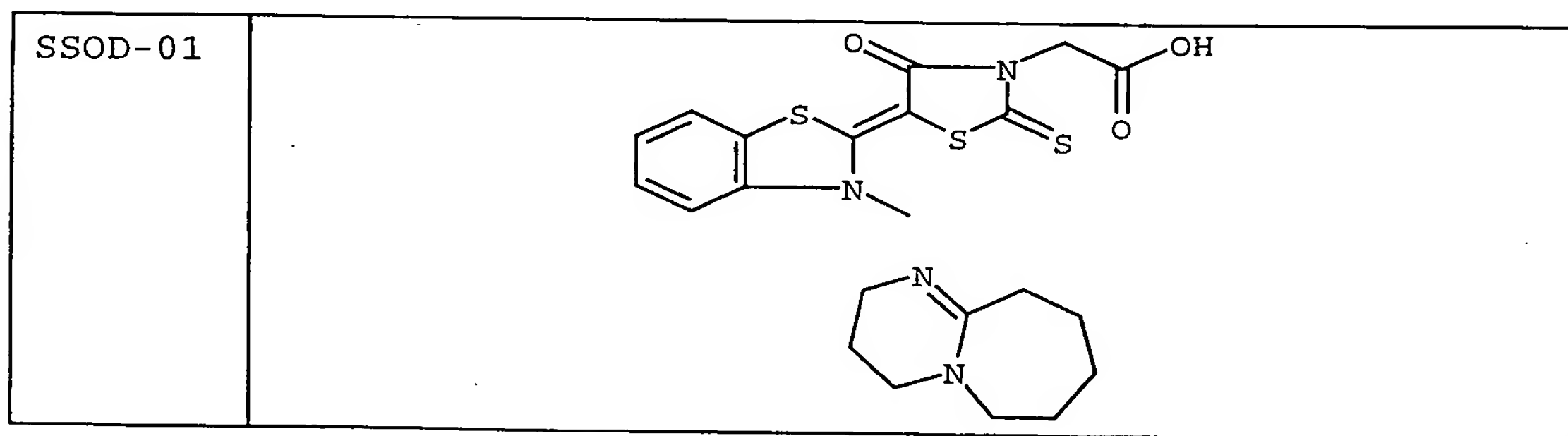
According to a tenth embodiment of the photovoltaic device, according to the present invention, the photovoltaic device further contains one or more metal sulphides nano-particles with a band-gap of less than 2.9 eV and greater than 1.5 eV.

35 According to an eleventh embodiment of the photovoltaic device, according to the present invention, the photovoltaic device further contains one or more metal chalcogenide nano-particles selected from the group consisting of lead sulphide, bismuth sulphide, cadmium sulphide, silver sulphide, antimony sulphide,
40 indium sulphide, copper sulphide, cadmium selenide, copper selenide, indium selenide and cadmium telluride.

Vogel et al. in 1990 in Chemical Physics Letters, volume 174, page 241, herein incorporated by reference, reported the sensitization of highly porous TiO_2 with in-situ prepared quantum size CdS particles (40-200Å), a photovoltage of 400 mV being achieved with visible light and high photon to current efficiencies of greater than 70% being achieved at 400 nm and an energy conversion efficiency of 6.0% under monochromatic illumination with $\lambda = 460$ nm. In 1994 Hoyer et al. reported in Applied Physics, volume 66, page 349, that the inner surface of a porous titanium dioxide film could be homogeneously covered with isolated quantum dots.

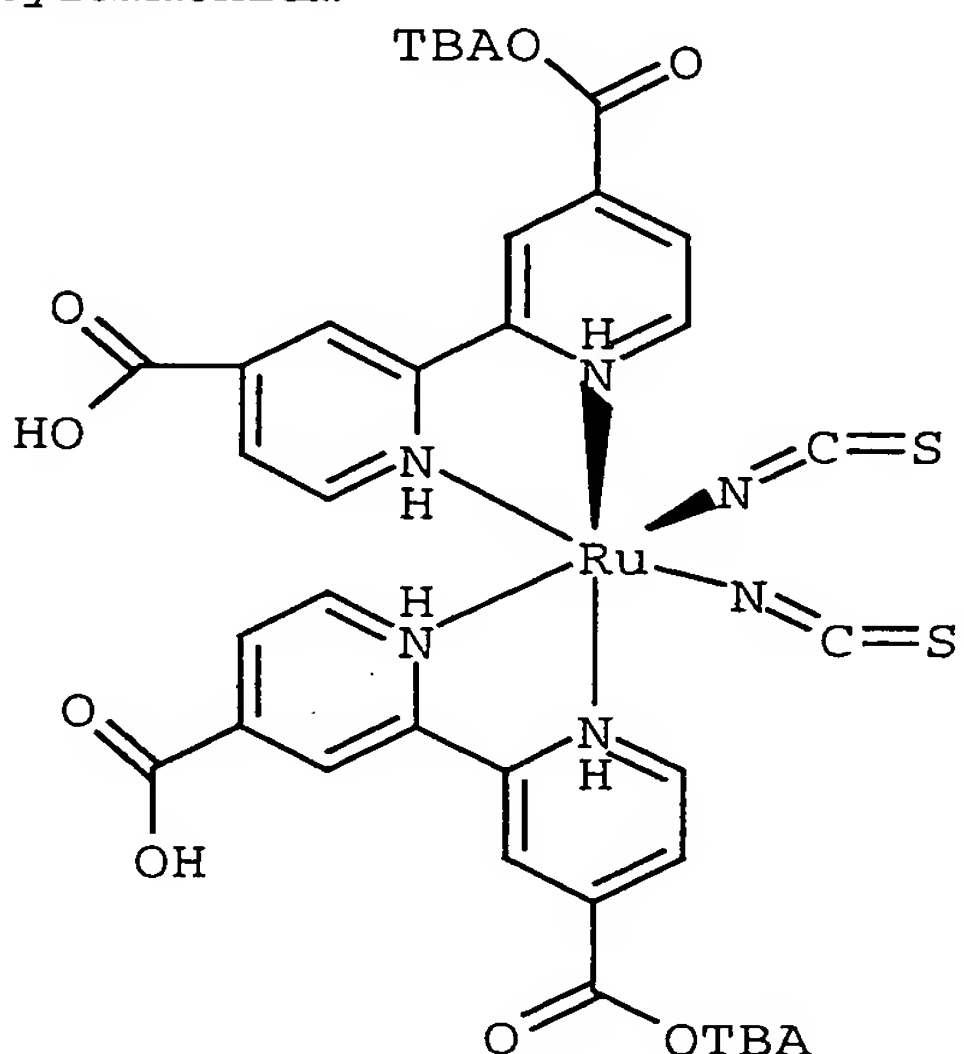
EP-A 1 176 646, herein incorporated by reference, discloses a solid state p-n heterojunction comprising an electron conductor and a hole conductor, characterized in that it further comprises a sensitizing semiconductor, said sensitizing semiconductor being located at an interface between said electron conductor and said hole conductor; and its application in a solid state sensitized photovoltaic cell. In a preferred embodiment the sensitizing semiconductor is in the form of particles adsorbed at the surface of said electron conductor and in a further preferred embodiment the sensitizing semiconductor is in the form of quantum dots, which according to a particularly preferred embodiment are particles consisting of PbS, CdS, Bi_2S_3 , Sb_2S_3 , Ag_2S , InAs, CdTe, CdSe or HgTe or solid solutions of HgTe/CdTe or HgSe/CdSe.

Suitable spectrally sensitizing organic dyes (SSOD) include cyanine, merocyanine and anionic dyes, such as:



SSOD-02	<p>Chemical structure of SSOD-02: A benzothiazine derivative. It features a benzene ring fused to a five-membered ring containing a sulfur atom and a nitrogen atom. The nitrogen atom is substituted with an ethyl group. The sulfur atom is part of a five-membered ring containing a carbonyl group and a sulfur atom. The sulfur atom is also part of a five-membered ring containing a nitrogen atom and a carboxylic acid group. A bicyclic amine structure is also shown below the main structure.</p>
SSOD-03	<p>Chemical structure of SSOD-03: A benzothiazine derivative. It features a benzene ring fused to a five-membered ring containing a sulfur atom and a nitrogen atom. The nitrogen atom is substituted with a carboxylic acid group. The sulfur atom is part of a five-membered ring containing a carbonyl group and a sulfur atom. The sulfur atom is also part of a five-membered ring containing a nitrogen atom and a carboxylic acid group. A benzene ring is also shown below the main structure.</p>
SSOD-04	<p>Chemical structure of SSOD-04: A benzothiazine derivative. It features a benzene ring fused to a five-membered ring containing a sulfur atom and a nitrogen atom. The nitrogen atom is substituted with a carboxylic acid group. The sulfur atom is part of a five-membered ring containing a carbonyl group and a sulfur atom. The sulfur atom is also part of a five-membered ring containing a nitrogen atom and a carboxylic acid group. A benzene ring is also shown below the main structure.</p>
SSOD-05	<p>Chemical structure of SSOD-05: A benzothiazine derivative. It features a benzene ring fused to a five-membered ring containing a sulfur atom and a nitrogen atom. The nitrogen atom is substituted with a carboxylic acid group. The sulfur atom is part of a five-membered ring containing a carbonyl group and a sulfur atom. The sulfur atom is also part of a five-membered ring containing a nitrogen atom and a carboxylic acid group. A benzene ring is also shown below the main structure.</p>

Suitable spectrally sensitizing metallo-organic dyes allowing for broad absorption of the solar spectrum include:

	chemical name
Ruthenium 470, a ruthenium dye from Solaronix	tris(2,2'-bipyridyl-4,4' dicarboxylato) ruthenium (II) dichloride
Ruthenium 505, a ruthenium dye from Solaronix	cis-bis(isocyanato) (2,2'-bipyridyl-4,4' dicarboxylato) ruthenium (II)
Ruthenium 535 (previously known as SRS-HQ, N3), a ruthenium dye from Solaronix	cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II)
Ruthenium 535 bis-TBA (previously known as MRS-HQ, N719, dye salt) a ruthenium dye from Solaronix	cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) bis-tetrabutylammonium 
Ruthenium 620 "Black Dye", a ruthenium dye from Solaronix	(anion only) tris(isothiocyanato)-ruthenium(II)-2,2':6',2''-terpyridine-4,4',4''-tricarboxylic acid

Process for preparing a photovoltaic device

Aspects of the present invention are realized by a process for
5 preparing a photovoltaic device, according to the present
invention, with at least one transparent electrode comprising the
steps of: providing a support with a conductive layer as one
electrode; coating the conductive layer on the support with a layer
comprising the n-type semiconductor with a bandgap of greater than
10 2.9 eV; coating the n-type semiconductor-containing layer with a
solution or dispersion comprising the 1,3,5-tris-aminophenyl-
benzene compound, or cation thereof, to provide after drying a
layer comprising the 1,3,5-tris-aminophenyl-benzene compound; and

applying a conductive layer to the layer comprising the 1,3,5-tris-aminophenyl-benzene compound thereby providing a second electrode.

According to a first embodiment of the process, according to the present invention, the solution or dispersion of the 1,3,5-tris-aminophenyl-benzene compound according to formula (I) or cation thereof further contains a binder.

According to a second embodiment of the process, according to the present invention, the solution or dispersion of the 1,3,5-tris-aminophenyl-benzene compound according to formula (I) or cation thereof further contains an electrolyte. Suitable electrolytes include $\text{Li}[(\text{CF}_3\text{SO}_2)_2\text{N}]$ and lithium trifluoromethanesulphonate (lithium triflate).

According to a third embodiment of the process, according to the present invention, the process further comprises the step of applying a solution or dispersion of a spectral sensitizer directly to the n-type semiconductor layer.

Support

Supports for use according to the present invention include polymeric films, silicon, ceramics, oxides, glass, polymeric film reinforced glass, glass/plastic laminates, metal/plastic laminates, paper and laminated paper, optionally treated, provided with a subbing layer or other adhesion promoting means to aid adhesion to the layer configuration, according to the present invention. Suitable polymeric films are poly(ethylene terephthalate), poly(ethylene naphthalate), polystyrene, polyethersulphone, polycarbonate, polyacrylate, polyamide, polyimides, cellulose triacetate, polyolefins and poly(vinylchloride), optionally treated by corona discharge or glow discharge or provided with a subbing layer.

Industrial application

Layers of nano-porous metal oxide semiconductors with a band-gap of greater than 2.9 eV prepared according the process, according to the present invention, can be used in both regenerative and photosynthetic photovoltaic devices.

The invention is illustrated hereinafter by way of reference and invention photovoltaic devices. The percentages and ratios given in these examples are by weight unless otherwise indicated.

Spiro-OMeTAD from SOLARONIX with the chemical name 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenyl-amine)-9,9'-spirobifluorene was used as a reference material to check if the basic recipe and the configuration of the cell were in order.

EXAMPLE 1

Photovoltaic devices with solid state organic hole conductor and high temperature sintered nano-porous TiO₂.

Photovoltaic devices 1 to 3 were prepared by the following procedure:

15 Preparation of the front electrode:

A glass plate (2 x 7 cm²) coated with conductive SnO₂:F (Pilkington TEC15/3) with a surface conductivity of ca. 15 Ohm/square was ultrasonically cleaned in isopropanol for 5 minutes and then dried.

A small strip of SnO₂:F was removed to prevent short circuit. The glass electrode was partially covered with glass on the long side and a dense non-porous hole blocking titanium dioxide layer applied by spray pyrolysis of an ethanolic solution of di-isopropoxy titanium-bis (acetylacetonate) in aerosol form as described by Kavan L. et al. In Electrochim. Acta (1995), 40(5), 643-52, herein incorporated by reference.

5 g of P25, a flame pyrolyzed nano-sized titanium dioxide with a mean particle size of 25 nm and a specific surface of 55 m²/g from DEGUSSA, was added to 15 mL of water followed by 1 mL of Triton X-100. The resulting titanium dioxide colloidal dispersion was cooled in ice and ultrasonically treated for 5 minutes. This dispersion was then doctor-blade coated onto the middle (0.7 x 4.5 cm²) of the electrode with the non-porous hole blocking titanium dioxide layer taped off at the borders. Nano-sized titanium dioxide dispersion-coated glass electrodes were heated at 450°C for 30 minutes then cooled to 150°C on a hot plate at 150°C for 10 minutes thereby yielding a nano-porous TiO₂ layer thickness of 2 µm. After cooling to 150°C, the nano-porous TiO₂ layer-coated glass electrode was immediately immersed in a 2 x 10⁻⁴ M solution of the Ruthenium 535 bis-TBA dye (from SOLARONIX) for 15 to 17 hours, followed by rinsing with acetonitrile to remove the non-adsorbed dye and drying

at 50°C for several minutes. The front electrode thereby produced was immediately used in assembling a photovoltaic cell.

Coating with layers of hole transporting materials:

Solutions of the hole transporting materials were prepared as follows:

HTM solution 1:

60 mg (53.1 μ moles) of Spiro-OMeTAD was dissolved in 200 μ l chlorobenzene (Aldrich) by heating for 1 hour at 70°C. 10.5 μ l of a solution of 56.7 μ g N(p-C₆H₄Br)₃SbCl₆ (69.4 nmoles) (Aldrich) and 907 μ g Li[(CF₃SO₂)₂N] (3.16 μ moles) (Fluka) in acetonitrile were then added to this solution to give a HTM solution 1 0.25M in Spiro-OMeTAD, 0.33mM in N(p-C₆H₄Br)₃SbCl₆ and 15mM in Li[(CF₃SO₂)₂N].

HTM solution 2:

35 mg (35.8 μ moles) of TABP01 was dissolved in 200 μ l chlorobenzene (Aldrich). To this solution, 10.5 μ l of a solution of 56.7 mg N(p-C₆H₄Br)₃SbCl₆ (69.4 nmoles) (Aldrich) and 907 mg Li[(CF₃SO₂)₂N] (3.16 μ moles) (Fluka) in acetonitrile was then added to the solution to give to give a HTM solution 2 0.17M in TABP01, 0.33mM in N(p-C₆H₄Br)₃SbCl₆ and 15mM in Li[(CF₃SO₂)₂N].

HTM solution 3:

35.4 mg (35.8 μ moles) of TABP03 was dissolved in 200 μ l chlorobenzene (Aldrich). To this solution, 10.5 μ l of a solution of 56.7 mg N(p-C₆H₄Br)₃SbCl₆ (69.4 nmoles) (Aldrich) and 907 mg Li[(CF₃SO₂)₂N] (3.16 μ moles) (Fluka) in acetonitrile was then added to the solution to give to give a HTM solution 2 0.17M in TABP03, 0.33mM in N(p-C₆H₄Br)₃SbCl₆ and 15mM in Li[(CF₃SO₂)₂N].

N(p-C₆H₄Br)₃SbCl₆ oxidized the charge transport compound to its cationic salt, Li[(CF₃SO₂)₂N] acting as an electrolyte. Sufficient N(p-C₆H₄Br)₃SbCl₆ was present to ensure that the oxidation process went to completion as determined spectrophotometrically by monitoring, in the case of TABP01, the 397 nm, 695 nm and 772 nm peaks of the cationic state in analogy to the absorption spectrum reported in 1994 by Bonvoisin et al. in Journal of Physical

Chemistry, volume 98, pages 5052-5057. Bonvoisin et al. reported that cyclic voltammetry and coulometry on TABP01 showed a unique, reversible, oxidation wave corresponding to a three-electron process, which was accompanied by the appearance of three bands at 397 nm, 695 nm and 772 nm respectively, corresponding to the tri-cation chromophore. TABP01 and TAPB03 appear to be oxidizable to their tri-cations i.e. all three nitrogens in the molecule are oxidizable, whereas in the case of Spiro-OMeTAD only two of the four nitrogens appear to be oxidizable.

10 The front electrode was placed on the spincoater, the cover was closed and a flow of Argon was fed in for 2 minutes. About 150 μ l of solution 1 was then dropped on the front electrode so as to cover the whole area. After waiting for 30 to 60 s for the drop to spread, the spincoater was again closed and again Argon flow was 15 fed in for 1 minute. It took 5 s for the spincoater to accelerate to 1000 rpm at which speed the solution was allowed to spin for 30 minutes.

The front electrode coated with the charge transport compound was then dried in the dark under Argon at 25°C for 30 minutes 20 followed by drying in a vacuum exicator for a further 30 minutes in dark. Finally a gold electrode was evaporated on top.

Measurements were only carried out after the photovoltaic device had stabilized in the dark at 25°C, which took between 1 and 24 hours. The same procedure was carried out for all six solutions. 25 This resulted in PV devices 1, 2 and 3.

Photovoltaic device characterisation

The photovoltaic device configuration is shown in Figure 1. 30 The cell was irradiated with a Steuernagel Solar Constant 575 solar simulator with a metal halide 1 AM light source. The simulator was adjusted to about 1 sun equivalent. The electricity generated was recorded with a Type 2400 SMU Keithley electrometer in the voltage range -1 to +1 volt.

35 Table 1 lists the short circuit current (I_{sc}) and open circuit voltage (V_{oc}) for the devices. The active area was 0.14 cm².

Table 1:

photovoltaic device	hole transporting material	Isc ($\mu\text{A}/\text{cm}^2$)	Voc (mV)
1 (ref.)	Spiro-OMeTAD	2880	795
2 (inv.)	TAPB01	11	585
3 (inv.)	TAPB03	4	475

Photovoltaic devices 2 and 3 with 1,3,5-tris-aminophenyl-benzene
5 compounds TAPB01 and TAPB03 in a tri-cationic form and heat
sintered titanium dioxide exhibit photovoltaic effects exhibit
photovoltaic effects.

EXAMPLE 2

10

Photovoltaic devices with solid state organic hole conductor and
high pressure sintered nano-porous TiO_2

Photovoltaic devices 4 to 6 were prepared by the following
15 procedure:

Photovoltaic devices 4 to 6 were prepared as described for
Photovoltaic devices 1 to 3, except that nano-titanium dioxide
dispersion-coated glass electrode was first dried at 110°C for 5
20 minutes, then, after cooling to room temperature, a pressure of 500
bars was applied for 5 seconds. This pressure sintered coating was
then heated to 150°C , immediately immersed in a 2×10^{-4} M solution
of the Ruthenium 535 bis-TBA dye and then washed and dried as
described for Photovoltaic devices 1 to 3.

25

Photovoltaic device 7 was prepared by the following procedure:

A $2 \times 7 \text{ cm}^2$ piece of ITO-coated (from IST) with a surface
resistivity of 70 Ohm/square was cleaned by rinsing in ethanol and
30 ozone treatment. The electrode was partially covered with adhesive
tape and put in an electron-beam apparatus. It was placed overnight
in a vacuum with continuous pumping and the non-porous TiO_2 was
applied locally to the substrate. After the deposition, the vacuum
was released and the sample was ready to use.

35 5 g of DEGUSSA P25 titanium dioxide nano-particles was added to
15 mL of water and the resulting titanium dioxide colloidal
dispersion cooled in ice and ultrasonically treated for 5 minutes.

This dispersion was then doctor-blade-coated onto the middle ($0.7 \times 4.5 \text{ cm}^2$) of the non-porous hole blocking titanium dioxide layer taped off at the borders.

The coated PET electrode with the nano titanium dioxide dispersion was first dried at 110°C for 5 minutes, then, after cooling to room temperature, a pressure of 500 bars was applied for 5 seconds. This pressure sintered coating was then heated to 150°C , immediately immersed in a $2 \times 10^{-4} \text{ M}$ solution of the Ruthenium 535 dye and the procedure described for Photovoltaic devices 1 to 3 followed. Finally layers of Spiro-OMeTAD and gold were applied as described for Photovoltaic device 1.

Table 2 lists the results for the different hole transporting materials with pressure sintered TiO_2 on a glass electrode and on an ITO-PET electrode.

Table 2:

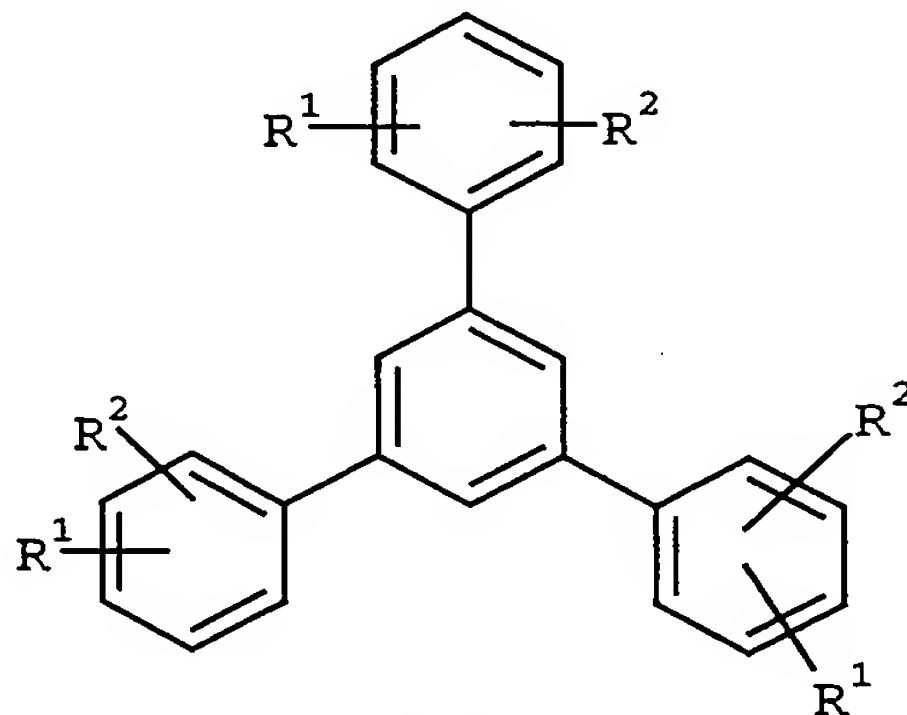
Photovoltaic device	Substrate	hole transporting material	Isc ($\mu\text{A}/\text{cm}^2$)	Voc (mV)
4 (ref.)	Glass/SnO2	Spiro-OMeTAD	20	735
5 (inv.)	Glass/SnO2	TAPB01	0.66	215
6 (inv.)	Glass/SnO2	TAPB03	0.71	385
7 (ref.)	PET/ITO	Spiro-OMeTAD	5	585

Photovoltaic devices 5 and 6 with 1,3,5-tris-aminophenyl-benzene compounds TAPB01 and TAPB03 in a tri-cationic form and pressure sintered titanium dioxide exhibit photovoltaic effects, which are much closer to the performance of the reference photovoltaic device with Spiro-OMeTAD than for photovoltaic devices with heat sintered titanium dioxide.

The present invention may include any feature or combination of features disclosed herein either implicitly or explicitly or any generalisation thereof irrespective of whether it relates to the presently claimed invention. In view of the foregoing description it will be evident to a person skilled in the art that various modifications may be made within the scope of the invention.

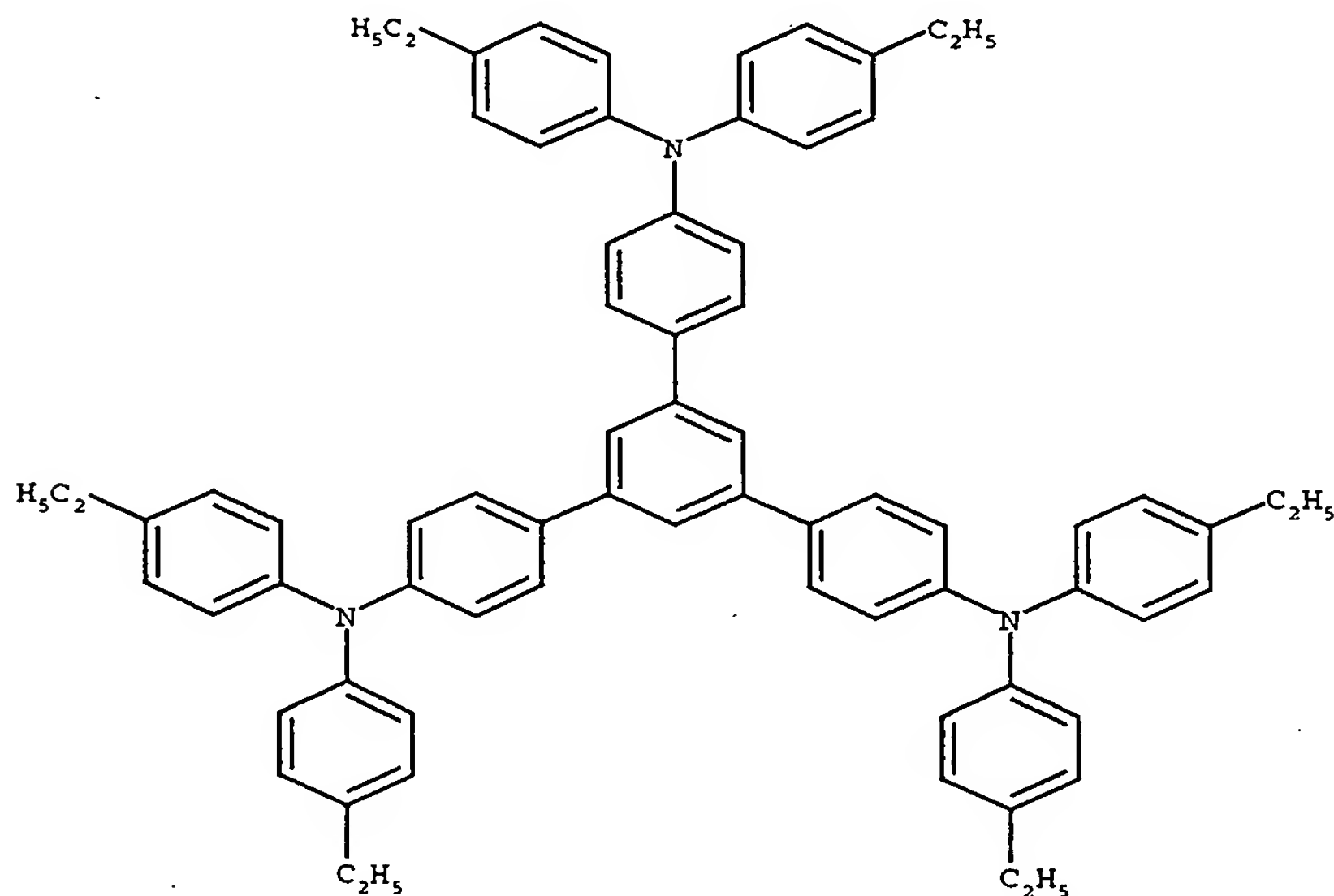
CLAIMS

1. A photovoltaic device comprising a n-type semiconductor with a band-gap of greater than 2.9 eV and a 1,3,5-tris-aminophenyl-benzene compound represented by formula (I):

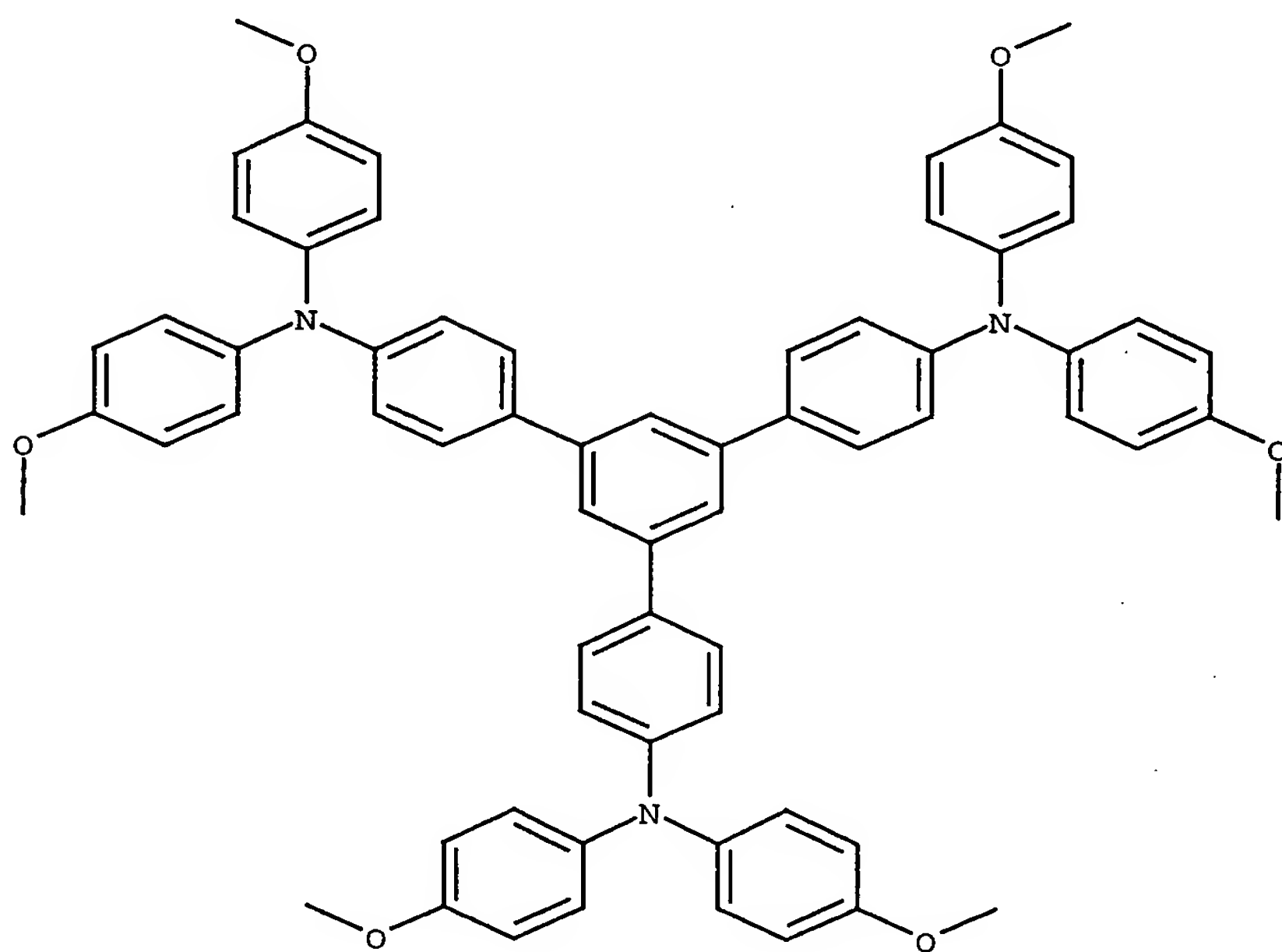
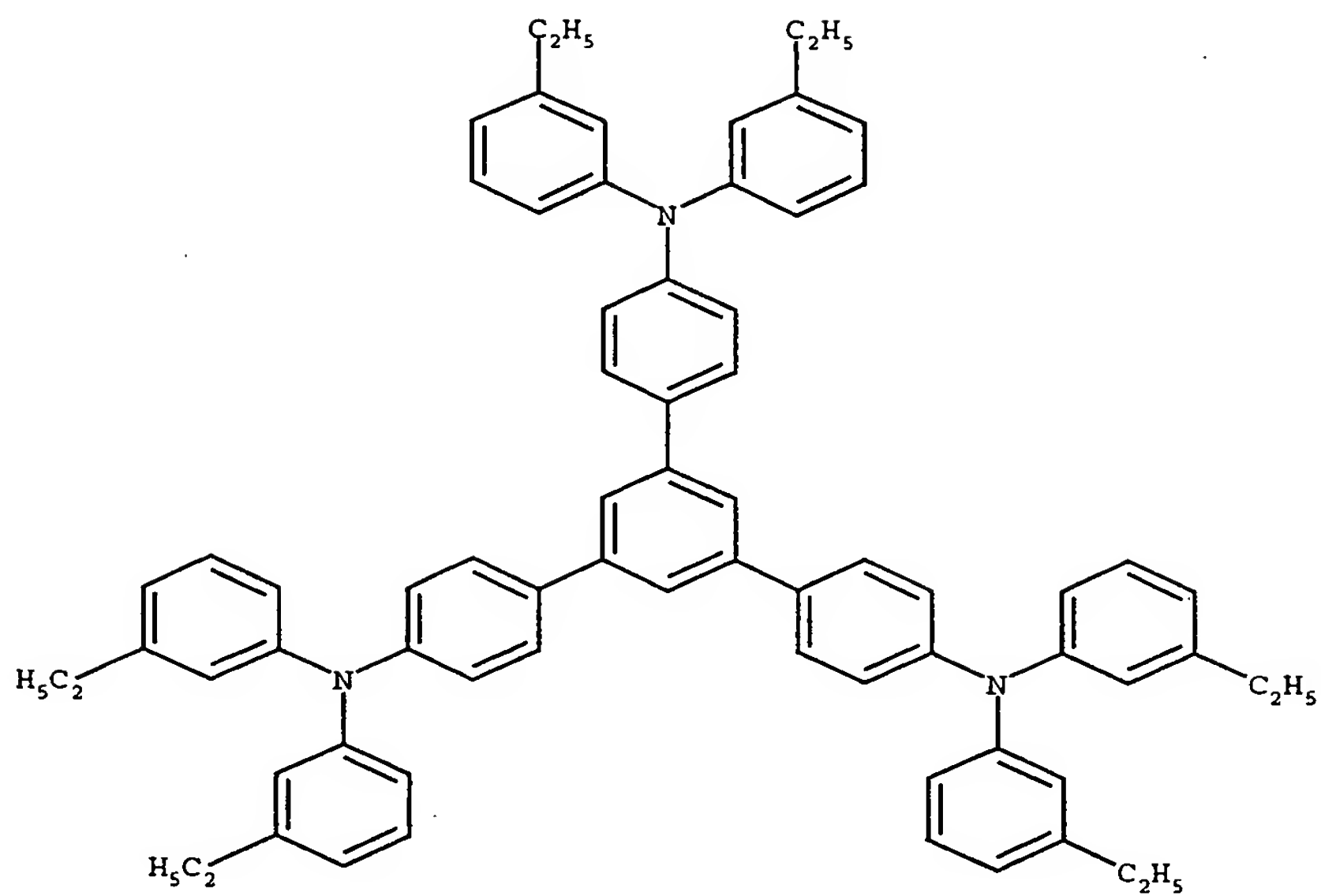


wherein R^1 represents a $-NR^3R^4$ group, wherein R^3 and R^4 , same or different, represents a C_2-C_{10} alkyl group including said alkyl groups in substituted form, a benzyl group, a cycloalkyl group, or an aryl group, and R^2 represents hydrogen, an alkyl group including a substituted alkyl group or halogen; and said 1,3,5-tris-aminophenyl-benzene compound is optionally in a cationic form.

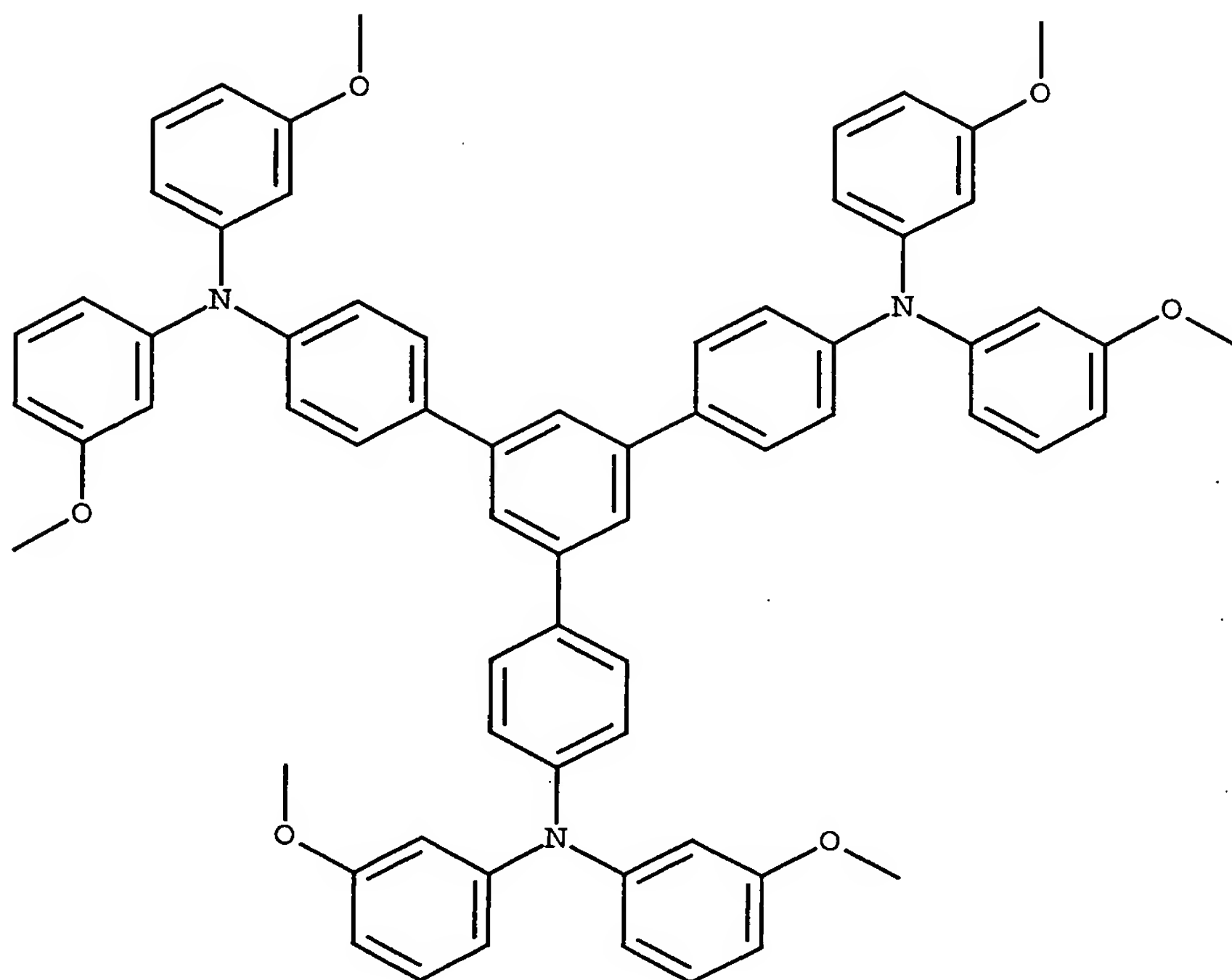
2. Photovoltaic device according to claim 1, wherein said 1,3,5-tris-aminophenyl-benzene compound represented by formula (I) is selected from the group consisting of:



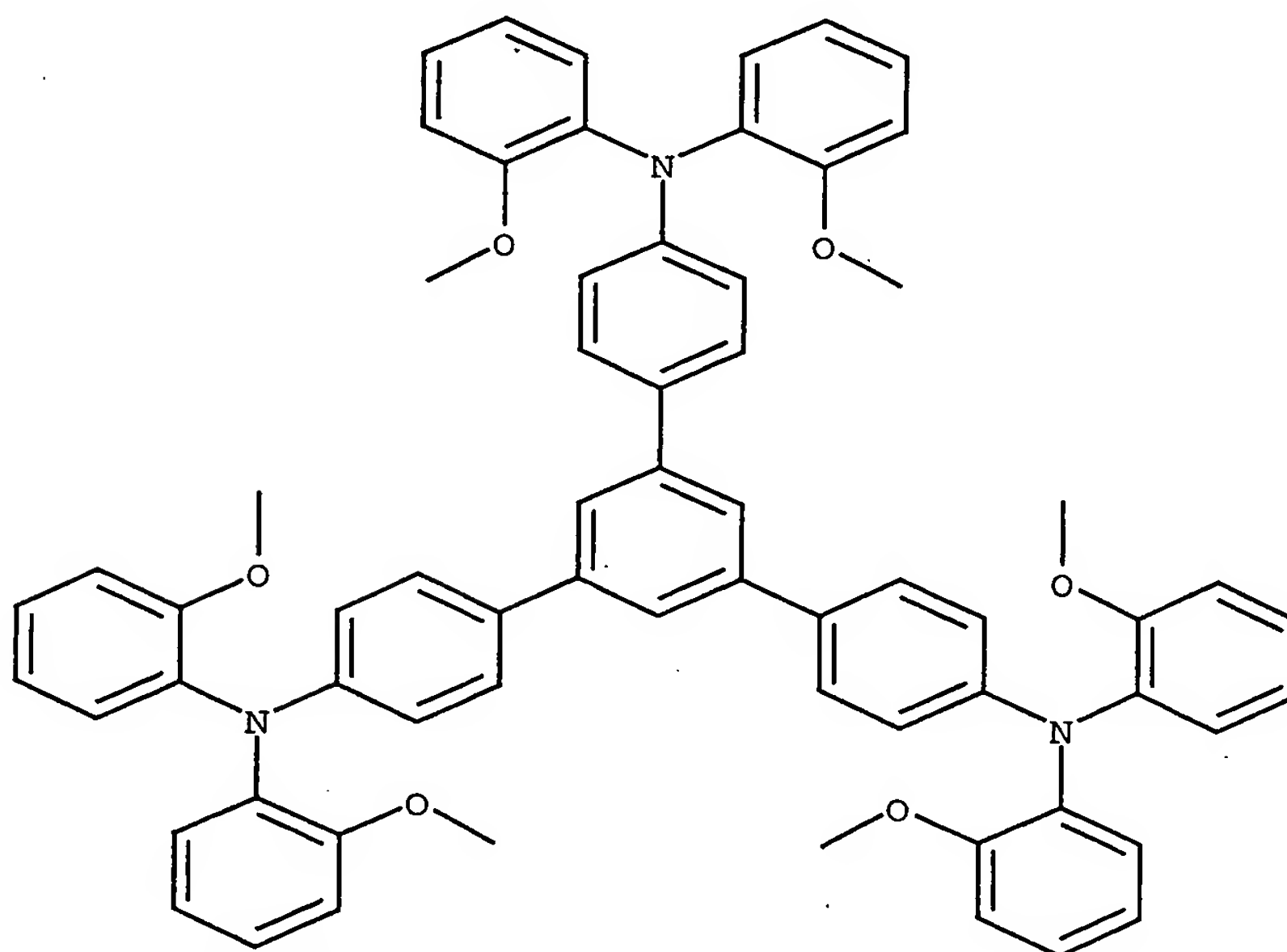
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and

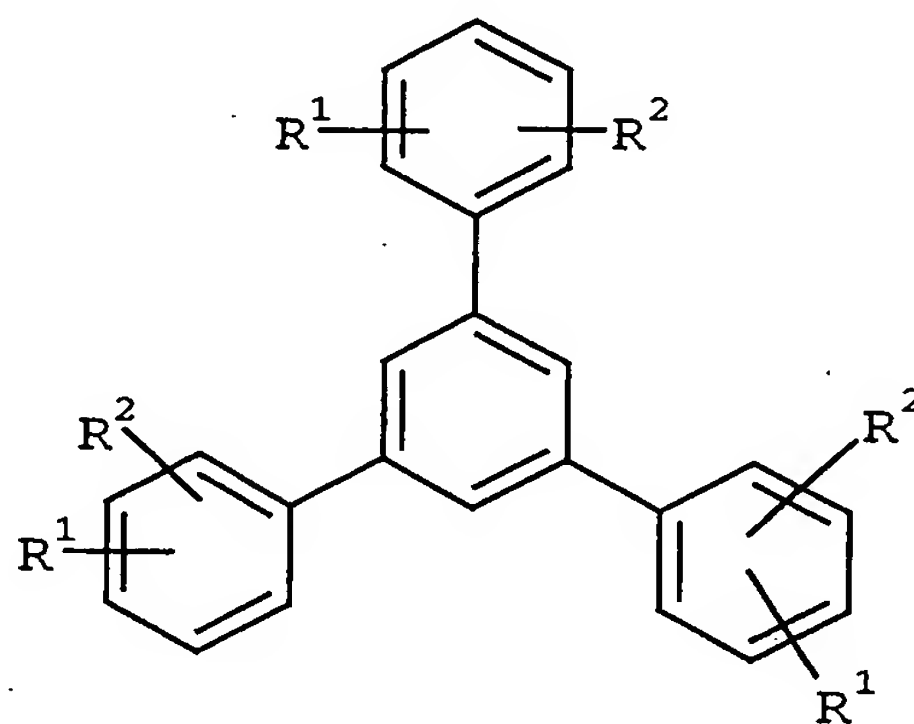


5 or the cations thereof.

3. Photovoltaic device according to claim 1, wherein said n-type semiconductor is selected from the group consisting of

titanium oxides, tin oxides, niobium oxides, tantalum oxides, tungsten oxides and zinc oxides.

4. Photovoltaic device according to claim 1, wherein said photovoltaic device further contains at least one spectral sensitizer.
5. Photovoltaic device according to claim 1, wherein said photovoltaic device further contains at least one spectral sensitizer selected from the group consisting of metal chalcogenide nano-particles with a band-gap of less than 2.9 eV, organic dyes and metallo-organic dyes.
6. Photovoltaic device according to claim 1, wherein said photovoltaic device further contains at least one spectral sensitizer selected from the group consisting metal oxides, metal sulphides and metal selenides.
7. A process for preparing a photovoltaic device comprising a n-type semiconductor with a band-gap of greater than 2.9 eV and a 1,3,5-tris-aminophenyl-benzene compound represented by formula (I):



wherein R^1 represents a $-NR^3R^4$ group, wherein R^3 and R^4 , same or different, represents a C_2-C_{10} alkyl group including said alkyl groups in substituted form, a benzyl group, a cycloalkyl group, or an aryl group, and R^2 represents hydrogen, an alkyl group including a substituted alkyl group or halogen, and said 1,3,5-tris-aminophenyl-benzene compound is optionally in a cationic form, with at least one transparent electrode comprising the steps of: providing a support with a conductive layer as one electrode; coating said conductive layer on the support with a layer comprising said n-type semiconductor with a bandgap of

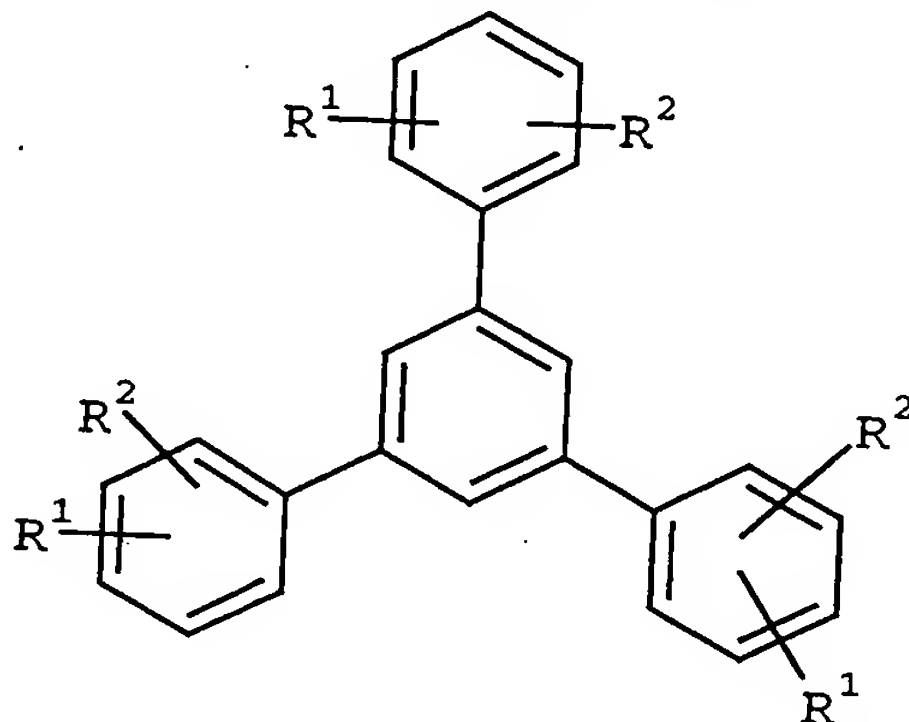
greater than 2.9 eV; coating said n-type semiconductor-containing layer with a solution or dispersion comprising said 1,3,5-tris-aminophenyl-benzene compound, or cation thereof, to provide after drying a layer comprising said 1,3,5-tris-aminophenyl-benzene compound; and applying a conductive layer to said layer comprising said 1,3,5-tris-aminophenyl-benzene compound thereby providing a second electrode.

ABSTRACT

PHOTOVOLTAIC DEVICE COMPRISING A 1,3,5-TRIS-AMINOPHENYL-BENZENE
COMPOUND OPTIONALLY IN A CATION FORM

5

A photovoltaic device comprising a n-type semiconductor with a band-gap of greater than 2.9 eV, a spectral sensitizer and a 1,3,5-tris-aminophenyl-benzene compound represented by formula (I):



10 wherein R¹ represents a -NR³R⁴ group, wherein R³ and R⁴, same or different, represents a C₂-C₁₀ alkyl group including the alkyl groups in substituted form, a benzyl group, a cycloalkyl group, or an aryl group, and R² represents hydrogen, an alkyl group including a substituted alkyl group or halogen; and the 1,3,5-tris-
15 aminophenyl-benzene compound is optionally in a cationic form; and a process for preparing the above-mentioned photovoltaic device with at least one transparent electrode comprising the steps of: providing a support with a conductive layer as one electrode; coating the conductive layer on the support with a layer comprising
20 the n-type semiconductor with a bandgap of greater than 2.9 eV; coating the n-type semiconductor-containing layer with a solution or dispersion comprising the 1,3,5-tris-aminophenyl-benzene compound, or cation thereof, to provide after drying a layer comprising the 1,3,5-tris-aminophenyl-benzene compound; and
25 applying a conductive layer to the layer comprising the 1,3,5-tris-aminophenyl-benzene compound thereby providing a second electrode.